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**Monographs on**  
**Inorganic & Physical Chemistry**

**THE**  
**MOLECULAR VOLUMES**  
**OF LIQUID**  
**CHEMICAL COMPOUNDS**

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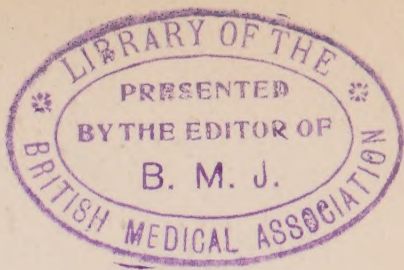


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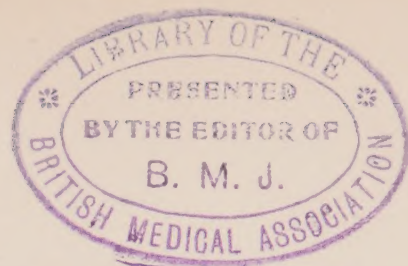
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## PREFACE.

THE work which has been attempted in the present volume is an application of the theory of molecular volumes from the point of view of Kopp, to a study of the constitutions of organic compounds chiefly. The working out of the theory thus reverts to the line of its historic development, the interval, representing a period of twenty-five years, marking no advance at all along this line. One reason is, that when the last important work was done, the question of the possible influence of constitutive influences on a physical property was not so prominent as it is to-day. The writers were, for the most part, content to point out that Kopp's additive rule suffered limitations, without inquiring into the reasons for this, and giving to the deviations their proper interpretation. We might, perhaps, except the work of Thorpe, which is thoroughly imbued with the modern spirit. It is, however, just these limitations of the additive rule which are so useful to the chemist in his endeavour to work out the details of the structure of chemical compounds. This has been turned to good account in most of the physical properties, and the success which has attended the work in these directions, has probably contributed to the comparative neglect of molecular volumes. Another reason is that, so long as Kopp's original values for carbon and hydrogen were retained, it was impossible to put the subject on a satisfactory basis, because, under the conditions, the evidence for one of the most important constitutive effects—that of ring structure—was completely obliterated. The following features of the old theory are retained: (*a*) Kopp's con-



ception of molecular and atomic volumes, and (b) the recognition of the additive principle. We are also indebted to those careful and patient workers, through whose laborious experimental researches that large amount of data which at present exists has accumulated. This has resulted in the detection of certain volume disturbances in the case of particular compounds the meaning of which was not at the time fully realized. These have of course been considered, and given what we believe to be their proper interpretation. Nearly all the atomic volumes have been modified; some are strikingly different from the old numbers. We also find it necessary to consider a larger number of atomic values for say, oxygen or nitrogen, than on the old theory. The result of these changes in the atomic values is a corresponding change in the conclusions drawn from the data. Whilst abundant material then existed for a fairly extended theory, it was found impossible to deal adequately with the subject, chiefly because of the initial errors in the values of the fundamental atoms, as well as on account of the imperfect conceptions of chemical constitution which then existed. We cannot claim to have elaborated a perfectly satisfactory system, but the initial mistakes have been corrected, and we believe that the work is progressing on the right lines. At least there has been an honest endeavour to correctly interpret facts, and we have not knowingly subjected the evidence to an undue strain.

The difficulties which one is likely to meet with in a research like the present one are great, for, owing to an *embarras des richesses*, one cannot at once distinctly perceive the relative importance of the facts which emerge, nor clearly distinguish real from imaginary regularities. Facts are liable to interpretation in so many ways. The want of an unifying principle has been keenly felt, but we believe that certain of the explanations which one feels instinctively to be slightly unsatisfactory, and which do not seem to fit in well with other explanations, are really



different aspects of one and the same thing. There are doubtless fundamental features which have not yet been grasped, and which might serve to link up facts at present somewhat disconnected.

Although we may have to wait for a thorough and scientifically worked out theory, we desire to lay stress on the good results which have already been obtained. The chief of these is undoubtedly the influence of ring structure and the evidence therefor. No physical property is apparently so well adapted to elucidate the ring structure of a compound as molecular volumes, and it is to be hoped that this will henceforward take its legitimate place among other physical properties as an instrument of research.

A study of molecular volumes, especially, has shown us that probably we are not at the end of the utility of physical properties as means for giving us an insight into the structure of molecules. When a more scientific method of examination of these physical properties shall have been worked out, there is no doubt that a great advance will be made in a knowledge of the intricacies of chemical constitution. It is doubtful if the possibilities in this direction are as yet generally realized.

Closely connected with the above subject, are a number of very important theoretical questions, such as the intimate structure of liquids, the nature of the atom and molecule, etc., but we have carefully avoided introducing these speculative questions into a more or less systematic work like the present.

We might, perhaps, note in passing, that the theory of molecular volumes, which is based upon an alternative conception of the structure of liquids, viz. : that due to Traube, has not been so successful as anticipated. An examination of current work shows how pessimistic is the spirit which obtains with reference to it. Thus we find in a recent textbook\* on physical chemistry, "Beyond the

\* *The Relations between Chemical Constitution and some Physical Properties*, by Dr. Smiles, chap. IV., pp. 145-6.

detection of association, volume relations are of little use in solving questions of constitution," and again, ". . . . The prospect of such a method is not very bright . . . ." Leaving aside the fact that Traube's theory is based upon a number of assumptions which are doubtful, we should note that it does not answer to the test of all theory, viz. utility as an instrument of research, and an accumulation of good results obtained. A theory, like a tree, should be estimated by the quantity and quality of its fruit. Hitherto the crop has not been extensive.

The data have been chiefly obtained from Clarke's *Constants of Nature*, Part I., the *Chemiker-Kalender*, and from many of the original papers to be found in the English and German scientific journals.

We desire to express our gratitude to Prof. W. J. Pope, F.R.S., for the kindly help and encouragement extended for a period of eight years or so, during which most of the matter included in the present volume has been in course of preparation.

G. LE B.

15 October, 1915.



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## CHAPTER I.

### THE VOLUMES OF ORGANIC COMPOUNDS AT THE MELTING-POINT.

#### Open Chain Compounds.

**The hydrocarbons :  $n$  paraffins, olefins, and acetylenes.  
The atomic volumes of carbon and hydrogen.**

THE highly constitutive nature of the melting-point probably makes it generally unsuitable as a condition of comparison of the molecular volumes of compounds. Nevertheless, in certain cases, where the effect of constitution is constant, some remarkable regularities have been observed, and since the results in general agree with those under other conditions, we may consider them to be significant.

In 1907 the author<sup>1</sup> dealt with a long series of normal paraffins  $C_nH_{2n+2}$ , and showed that the volumes of the compounds in the liquid state, at the melting point, form an approximately arithmetical series, similar to that of their valencies. Thus if  $V_m$  represent the molecular volume of a member of the series  $C_nH_{2n+2}$ , under the conditions, and  $W$  the sum of the valencies,  $-C=4$ ,  $H=1$ —then the ratio  $V_m/W$  is constant, and equal to 2.970 approximately. This is one-sixth of the difference for  $CH_2$ , viz. 17.82.

The data are those of Krafft,<sup>2</sup> who also showed that the difference for  $CH_2$  is constant, and equal to 17.80.

TABLE I.—THE VOLUMES OF THE NORMAL PARAFFINS.

Hydrocarbons.	W.	M. Vol. = $V_m$ .	$\Delta$ for $\text{CH}_2$ .	$V_m/W = S.$	$W \times 2.970$ = M. Vol.
Undecane . . . $\text{C}_{11}\text{H}_{24}$	68	201.4		2.962	201.96
Dodecane . . . $\text{C}_{12}\text{H}_{26}$	74	219.9	18.5	2.971	219.78
Iridecane . . . $\text{C}_{13}\text{H}_{28}$	80	237.3	17.4	2.966	237.6
Tetradecane . . . $\text{C}_{14}\text{H}_{30}$	86	255.4	18.1	2.970	255.42
Pentadecane . . . $\text{C}_{15}\text{H}_{32}$	92	273.2	17.8	2.970	273.24
Hexadecane . . . $\text{C}_{16}\text{H}_{34}$	98	291.2	18.0	2.971	291.06
Heptadecane . . . $\text{C}_{17}\text{H}_{36}$	104	309.0	17.9	2.971	308.88
Octadecane . . . $\text{C}_{18}\text{H}_{38}$	110	326.9	17.9	2.972	326.70
Nonadecane . . . $\text{C}_{19}\text{H}_{40}$	116	344.7	17.8	2.971	344.52
Eicosane . . . $\text{C}_{20}\text{H}_{42}$	122	362.5	17.8	2.971	362.34
Heneicosane . . . $\text{C}_{21}\text{H}_{44}$	128	380.3	17.8	2.971	380.16
Docosane . . . $\text{C}_{22}\text{H}_{46}$	134	398.3	18.0	2.972	398.00
Tricosane . . . $\text{C}_{23}\text{H}_{48}$	140	416.2	17.9	2.971	415.8
Tetracosane . . . $\text{C}_{24}\text{H}_{50}$	146	434.1	17.9	2.971	415.8
Heptacosane . . . $\text{C}_{27}\text{H}_{56}$	164	487.4	$3 \times 17.8$	2.973	433.62
Hentriacontane . . . $\text{C}_{31}\text{H}_{64}$	188	558.4	$4 \times 17.75$	2.972	487.08
Dotriacontane . . . $\text{C}_{32}\text{H}_{66}$	194	576.2	17.8	2.970	558.36
Pentriacontane . . . $\text{C}_{35}\text{H}_{72}$	212	629.5	$3 \times 17.8$	2.970	576.18
Mean Values . . . . .			$\left\{ \begin{array}{l} 17.83 \\ = 6 \times 2.971 \end{array} \right.$	2.970	

The above simple relation may be interpreted as follows:—

(a) The volumes of the atoms, carbon and hydrogen are respectively the same in the individual compounds, but if only a slight change occurs from compound to compound, these volumes may be demonstrated by a comparison of a series of volumes.

(b) The volumes of carbon and hydrogen are

$$[\text{H}] = 2.970 \text{ and } [\text{C}] = 4 \times 2.970 = 11.88,$$

and the relation (1 : 4) between these, is similar to that existing between the valencies of carbon and hydrogen. The above numbers are of course only average ones, but there is evidence of only very small apparent deviations therefrom.

$$\text{Also } [\text{CH}_2] = 11.88 + 5.94 = 17.82.$$

*Direct Calculation of the Atomic Volumes of Carbon and Hydrogen.*

$$\begin{aligned} 2[\text{H}] &= [\text{C}_{15}\text{H}_{32}] + [\text{C}_{16}\text{H}_{34}] - [\text{C}_{31}\text{H}_{64}] \\ &= 273.2 + 291.2 - 558.4 = 6.0 \end{aligned}$$

$$2[\text{H}] = [\text{C}_{18}\text{H}_{38}] - 18[\text{CH}_2] = 326.9 - 18 \times 17.83 = 5.96.$$

The volume of hydrogen is thus very nearly equal to 3.0.

$$\text{Also } [\text{C}] = [\text{CH}_2] - 2[\text{H}] = 17.83 - 6.0 = 11.83.$$



The relation between these values is

$$\frac{[C]}{[H]} = \frac{11.83}{3.0} = 4.0 \text{ (approx.)}.$$

These data give us the means of calculating the volumes of the hydrocarbon elements in compounds at the melting-point.

$$\begin{aligned} [C_nH_{2n+2}] &= n[C] + (2n + 2)[H] \\ &= (6n + 2)[H] = (6n + 2) \times 2.970. \end{aligned}$$

Such values are found in the last column of the previous table.

Krafft studied the molecular volumes of the above paraffins, not only at the melting-points, but also at a number of temperatures up to 100°C. This enables us to compare the volumes of the paraffins at any temperature within these limits by making use of interpolation formulæ<sup>3</sup> of the type—

$$d_T = d_{T^1} \{ - \alpha t \pm \beta t^2 \}, \text{ where } t = T - T^1.$$

The results are recorded in the following table:—

TABLE II.—VALUES OF  $V_m/W$  ILLUSTRATING THE ADDITIVE RULE.

M.P. + $n \times 10$	$C_{12}H_{26}$	$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$	$C_{17}H_{36}$	$C_{18}H_{38}$
M.P. . .	2.971	2.966	2.970	2.970	2.971	2.971	2.972
„ + 10°	2.997	2.993	2.994	2.997	3.000	2.998	2.999
„ + 20°	3.025	3.020	3.023	3.024	3.027	3.025	3.026
„ + 30°	3.053	3.049	3.051	3.052	3.054	3.053	3.053
„ + 40°	3.081	3.078	3.081	3.080	3.082	3.081	3.082
„ + 50°	3.111	3.107	3.109	3.109	3.111	3.110	3.109
„ + 60°	3.141	3.137	3.139	3.140	3.140	3.138	3.137
„ + 70°	3.172	3.168	3.170	3.169	3.170	3.166	3.166
„ + 80°	3.206	3.200	3.201	3.200	3.201	—	—
„ + 90°	3.240	3.232	3.234	—	—	—	—

The above table shows that, at equal intervals of temperature from the melting-points, and in the liquid state, the volumes of the compounds are related to each other in a similar way to that at the melting-points.

The effect of homology, or the effect of want of strict similarity between the volumes of the atoms in the different terms of the series, is here at a minimum, and is in contrast to what we find under other conditions, such as the boiling-point. The nearly accurate manifestation of the additive rule extends to the neighbourhood of 100°, but under the latter condition there are signs of a slight relative expansion among the more complex members of the series.

### I. The Influence of the Alternating Factor.

If the differences for  $\text{CH}_2$ , as also the values  $V_m/W$ , be examined (see Table I), it will be found that they alternate in a remarkable way among the earlier members of the series. This is also found to be true of the melting-points, as was first pointed out by Baeyer<sup>4</sup> in the case of the fatty acids and other series. This is, however, a feature hitherto unrecognized in molecular volumes, and it is evident that the peculiarity which causes the melting-points of successive terms to alternate, also similarly affects the molecular volumes. The data for compounds simpler than undecane have been calculated by extrapolation from Krafft's data (loc. cit.), with the result that the effect has been traced to simpler compounds, where it is more marked. The melting-points of nonane  $\text{C}_9\text{H}_{20}$  and decane  $\text{C}_{10}\text{H}_{22}$  are  $-51^\circ\text{C}$ . and  $-25^\circ\text{C}$ . respectively.

TABLE III.—THE EFFECT OF THE ALTERNATING FACTOR ON THE MOLECULAR VOLUMES OF THE LIQUID NORMAL HYDROCARBONS.<sup>5</sup>

Substance.	W.	$V_m$ at m.p.	$\Delta$ .	$\Delta$ between <i>Odd</i> Members.	$\Delta$ between <i>Even</i> Members.	$V_m/W$ .	$V_m/W$ .
$\text{C}_9\text{H}_{20}$	56	165.67	18.9	35.7	35.4	2.957	—
$\text{C}_{10}\text{H}_{22}$	62	184.54	16.9			—	2.976
$\text{C}_{11}\text{H}_{24}$	68	201.40	18.5	35.9	35.5	2.962	—
$\text{C}_{12}\text{H}_{26}$	74	219.90	17.4			—	2.972
$\text{C}_{13}\text{H}_{28}$	80	237.30	18.1	35.9	35.8	2.966	—
$\text{C}_{14}\text{H}_{30}$	86	255.40	17.8			—	2.970
$\text{C}_{15}\text{H}_{32}$	92	273.20	18.0	35.8		2.970	—
$\text{C}_{16}\text{H}_{34}$	98	291.20	17.8			—	2.971
$\text{C}_{17}\text{H}_{36}$	104	309.00				2.971	—

It is apparent from the above table, that a difference in volume exists between the odd and even members of the hydrocarbon series below hexadecane  $\text{C}_{16}\text{H}_{34}$ .

The *odd* members of the series have relatively small volumes, but this depression gradually disappears as we ascend the series,



for in the table, the values of  $V_m/W$  gradually increase to a constant value—2.971.

The *even* members of the series have relatively large volumes, and this abnormal expansion gradually diminishes as the series is ascended until at about hexadecane  $C_{16}H_{34}$  the value of  $V_m/W$  is constant, or nearly so.

It follows that the values of  $V_m/W$ , which respectively refer to the odd and even terms of the series, can be arranged along two curves, which respectively represent values which are either depressed below, or raised above those which would belong to a mean curve, or one for which  $V_m/W$  is consistently 2.971. The two curves are practically coincident with each other, and with the mean condition, after  $C_{16}H_{34}$ . The alternating factor thus exerts an opposite effect on an odd or even member, of the series, these respectively possessing an odd and even number of carbon atoms in the chain.

The influence of the alternating factor upon the volume follows as a direct consequence of its effect upon the melting-point. We have no reason to suppose that this alternating factor, which may be considered to be due to a specific property of the molecules, specially affects the liquid volumes, but is only rendered evident by differences between the melting-points. Since the volumes are a function of temperature, they would naturally also be affected. The result is, that the melting-points of the odd numbers of the series are depressed and the volumes diminished below a mean condition, whilst the melting-points of the even members are elevated, and the volumes augmented above this mean condition. The phenomenon just noted is doubtless connected with the question of residual affinity. The members of the even series evidently require a higher temperature for the odd series in order to cause those changes which make possible a relative motion of the molecules. Beyond this we know very little. Biach<sup>6</sup> has endeavoured to account for the alternating effects apparent in the melting-points of other series by means of residual affinity. If we suppose that every pair of  $CH_2$  groups in the chains partially compensate each other, we see that there would be an excess of residual affinity when the number is odd, and a defect when even. This would cause a relative rise in boiling point and diminution in volume in the case of the first, and *vice versa*.

### The Effect of Unsaturation on the Molecular Volume at the Melting-Point.<sup>7</sup>

The detection of such a constitutive feature as the influence of the alternating factor, suggests the possibility of unsaturation under similar conditions, influencing molecular volumes. Fortunately the data are at hand to put this question to the test. These refer to the olefins  $C_nH_{2n}|=|$  and the acetylenes  $C_nH_{2n-2}|\equiv|$ , and are due to Krafft.<sup>8</sup> It will be convenient to draw our conclusions simply from the differences, because the value of  $CH_2$  is the same in the unsaturated series as in the normal paraffins. This shows that the saturated atoms possess similar volumes in saturated and unsaturated compounds, and that thus the effect of unsaturation is only local.

TABLE IV.—THE VALUE OF THE EFFECT FOR UNSATURATION.

Substance.	$V_m$ at m.p.	$\Delta$ .	Substance.	$V_m$ at m.p.	$\Delta$ .
Dodecane $C_{12}H_{26}$	219.9	8.7 6.2	Hexadecane $C_{16}H_{34}$	291.4	8.5 6.8
Dodecylene $C_{12}H_{24} = $	211.2		Hexadecylene $C_{16}H_{32} = $	282.9	
Dodecylidene $C_{12}H_{22} \equiv $	205.0		Hexadecylidene $C_{16}H_{30} \equiv $	276.1	
Tetradecane $C_{14}H_{30}$	255.4	8.5 6.4	Octadecane $C_{18}H_{38}$	326.9	8.3 6.8
Tetradecylene $C_{14}H_{28} = $	246.9		Octadecylene $C_{18}H_{36} = $	318.6	
Tetradecylidene $C_{14}H_{26} \equiv $	240.5		Octadecylidene $C_{18}H_{34} \equiv $	311.8	

It is apparent that unsaturation exerts a special effect on the molecular volumes under the above conditions. This is doubtless to be expected, since the molecules at the melting-point acquire characters of fixity which precludes relative motion, and because the molecular centres are less than at, say, the boiling-point.

If we compare the volumes of the corresponding members of any two series, we shall find that the differences are the same throughout, and that those which exist between any two of the terms in the three series are respectively some multiple of 17.8. These facts indicate (*a*) that the effect of single and double unsaturation is constant, and (*b*) that the atomic volumes of carbon and hydrogen are the same in the three series.

The effects due to unsaturation are calculated thus:—



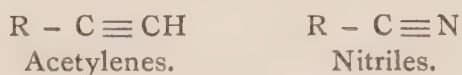
$$\begin{aligned}
 & - 2[\text{H}] + [ = ] \\
 & = [\text{C}_n\text{H}_{2n} | = | - \text{C}_n\text{H}_{2n+2}] = - 8.5 \\
 & \text{But } 2[\text{H}] = 2 \times 2.970 = 5.94. \\
 & \text{Therefore } [ = ] = - 8.5 + 5.94 = - 2.56. \\
 & \text{Also } - 4[\text{H}] + [ \equiv ] \\
 & = [\text{C}_n\text{H}_{2n-2} | \equiv | - \text{C}_n\text{H}_{2n+2}] - = 15.1 \\
 & \text{But } 4[\text{H}] = 11.9 \\
 & \therefore [ \equiv ] = - 15.1 + 11.9 = - 3.2.
 \end{aligned}$$

The depression caused by an olefin linkage  $| = |$  is equal to  $- 2.56$ , and that for an acetylene linkage  $| \equiv |$  is  $- 3.2$ .

These results show that a special effect due to unsaturation is observable at the melting-point, and this is in agreement with the conclusions drawn from the observation of other physical properties. One difference, however, is that, whereas, in optical refractivity and magnetic rotatory power, an *increase* in the magnitudes of the constants is observable, in molecular volumes on the other hand a *decrease* is noticed. These differences are what we should expect. It is to be supposed that the nearer that absolute zero is approached, constitutive effects like these become more marked. There is also the possibility that at the boiling-point, when the distance between the molecular centres is greater than at the melting-point, the effect for unsaturation may disappear altogether. The melting point is a highly constitutive property, and these temperatures are not related to each other in the same way as the boiling points of compounds. For this reason, the volumes referred to the melting-point, are not as a rule comparable with those referred to the boiling-point. The constitutive factors vary least from compound to compound, among the normal paraffins.

### The Nitriles.

In addition to the hydrocarbons, and particularly the unsaturated ones, Krafft<sup>9</sup> has also studied the alkyl cyanides or nitriles at the melting-point. They are unsaturated in a similar sense to the acetylenes, as a comparison of their formulæ will show.



The volume of combined nitrogen is—

$$[ \equiv \text{N} ] = 3[\text{H}].$$

On this assumption, we shall see from the following table, that there is an outstanding difference for unsaturation, on comparing the observed and the calculated values.

TABLE V.—THE VOLUMES OF THE NITRILES.  
R — C $\equiv$ N.

Substance.	W(R).	V <sub>m</sub> .	$\Delta$ for CH <sub>2</sub>	Vol. R.	— C $\equiv$ N.
Lauroitrile C <sub>11</sub> H <sub>23</sub> C $\equiv$ N	67	216.8		199.0	17.8
Myristonitrile C <sub>13</sub> H <sub>27</sub> C $\equiv$ N	79	252.3	35.5	234.6	17.7
Palmitonitrile C <sub>15</sub> H <sub>31</sub> C $\equiv$ N	91	288.2	35.9	270.3	17.9
Stearonitrile C <sub>17</sub> H <sub>35</sub> C $\equiv$ N	103	324.0	35.8	305.9	18.1
Mean Values . . .			$\left\{ \begin{array}{l} 35.7 \\ = 2 \times 17.85 \end{array} \right.$		17.87

The group — C $\equiv$ N evidently equals that of CH<sub>2</sub> in volume. On the assumption that

$$\begin{aligned} [C] &= 4[H] \text{ and } [N] = 3[H] \\ -C\equiv N &= 7[H] = 20.8 \text{ (calc.)} \\ \Delta \text{ for } |\equiv| &= 17.87 - 20.8 = -2.93. \end{aligned}$$

### Oxygen Compounds: Ketones and Fatty Acids.

(Krafft, loc. cit.)

#### *Hydroxylic Oxygen* (OH).

The melting-point is a physical property very sensitive to constitutive influences, and it is necessary to obtain the substance quite pure in order to show a melting sharply at one temperature. Slight traces of impurity are a serious impediment to an accurate determination. Some impurities are particularly difficult to get rid of, such as small quantities of substances belonging to the same series as that of the compound which is being examined. It follows that an accurate study of molecular volumes is dependent on an accurate estimation of the melting-points of the substances. How far the discrepancies, observed in a study of the molecular volumes, are due to such inaccuracies, it is difficult to say, but some may be due, at least in part, to this cause.

In drawing up a table of the alcohols we assume, what is very probable, that in each compound the atom of hydroxylic oxygen is equal in volume to twice that for a single hydrogen atom in the same compound, i.e.

$$[O'] = 2[H].$$



TABLE VI.—THE NORMAL ALCOHOLS.

Le Bas (loc. cit.).

Compound.			W.	$V_m$ .	$V_m/W$ .	$W \times S$ $S = 2.970$ .
Nonyl	Carbinol	$C_{10}H_{21}OH$	64	188.3	2.943	190.08
Undecyl	,,	$C_{12}H_{25}OH$	76	223.9	2.946	225.72
Tridecyl	,,	$C_{14}H_{29}OH$	88	259.8	2.953	261.36
Pentadecyl	,,	$C_{16}H_{33}OH$	100	296.0	2.960	297.00
Heptadecyl	,,	$C_{18}H_{37}OH$	112	332.3	2.970	332.64

An examination of the numbers shows that it is only at about heptadecyl carbinol that the value of  $V_m/W$  approximates to the normal value of 2.970.

There is a variation in the volumes as we ascend the series, which variation may be considered to be similar to those which we find at the boiling-point and due to the addition of the homologous increment  $CH_2$ . The significance of this probably is that, for the particular series in question, the compounds are not quite comparable at the melting-point. This want of correspondence between the two series—the melting-points and the molecular volumes—involves a difference between the volumes of the carbon and hydrogen atoms in the compounds from their usual values, derived from the normal paraffin series. The temperatures at which the volumes of these atoms are normal, are evidently not the melting-points. The value of hydrogen which has been noted, viz. : 2.970, is, however, likely to occur at the melting-point at some point of the series which is being examined. Among the alcohols, this occurs at heptadecyl carbinol  $C_{18}H_{37}OH$ .

#### *Ketonic Oxygen (C : O).*

The melting-points of the compounds of this series show signs of alternation, and this fact may possibly influence the molecular volumes somewhat.

The data, except for the more complex compounds, are of miscellaneous origin. The latter are due to Krafft (loc. cit.).

It is remarkable that, whilst the simpler compounds show values of  $V_m/W$ , which fall below the normal value 2.970, the

most complex show values which are in excess of this. Compounds of the complexity of  $(C_6H_{13})_2C : O$ , in their results, are similar to those of the paraffin series, in that the values of  $V_m/W$  are  $= 2.970$  exactly.

$$[O''] = 3[H] = 3 \times 2.970 = 8.91.$$

TABLE VII.—THE VOLUMES OF THE KETONES.

W.	Compound.	m.p.	$V_m$ .	$\Delta$ .	$W \times 2.970$ .	$\Delta$ .
63	$C_8H_{17} \cdot CO \cdot CH_3$	3.5	186.2	—	187.1	+0.9
69	$C_9H_{19} \cdot CO \cdot CH_3$	15.0	204.4	—	204.9	+0.5
69	$C_5H_{11} \cdot CO \cdot C_5H_{11}$	14.6	204.3	—	204.9	+0.6
81	$C_6H_{13} \cdot CO \cdot C_6H_{13}$	28.0	240.6		240.6	—
93	$C_7H_{15} \cdot CO \cdot C_7H_{15}$	40.0	276.2	35.6 $2 \times 17.8$ 35.8	276.2	—
105	$C_8H_{17} \cdot CO \cdot C_8H_{17}$	49.0	312.0		311.8	-0.2
141	Laurone . . . . . $C_{11}H_{23} \cdot CO \cdot C_{11}H_{23}$	69.0	420.6	—	418.8	-1.8
165	Myristone . . . . . $C_{13}H_{27} \cdot CO \cdot C_{13}H_{27}$	76.3	491.7	71.1 $4 \times 17.8$	490.0	-1.7
189	Palmitone . . . . . $C_{15}H_{31} \cdot CO \cdot C_{15}H_{31}$	82.8	562.7	71.0	561.3	-1.4
213	Stearone . . . . . $C_{17}H_{35} \cdot CO \cdot C_{17}H_{35}$	88.4	634.3	71.6	632.6	-1.7
Mean value . . . . .				$\left\{ \begin{array}{l} 71.2 \\ = 17.8 \times 4 \end{array} \right.$		

It is probable, from the evidence of the above numbers, that the series of melting-points and the series of temperatures for which the volumes of similar atoms are equal, are not quite the same. We notice that the differences between the calculated and observed molecular volumes for laurone, etc., are the same, viz. 1.70.

The following results show that

$$[O''] = 3[H]$$

in the ketones, and that the apparent deviations therefrom, are due to disturbances of the total volumes of the compounds, for some reason similar to that already stated.

				$V_m$	$O''$
$[C_{15}H_{30}O]$	+	$2[H]$	=	282.17	
$[C_{15}H_{32}]$			=	273.2	8.97
and $[C_{17}H_{34}O]$	+	$2[H]$	=	317.97	
$[C_{17}H_{34}]$			=	309.0	8.97



This is sufficiently near to  $8.91 = 3 \times 2.970 = 3H$  to make it probable that the volume of  $O'$  in the ketones is in reality equal to  $3H$ .

*Carboxylic Oxygen C : O (OH).*

The fatty acids  $C_nH_{2n}O_2$  are subject to the alternating factor, but sufficient data do not exist for a study of this subject in relation to them.

Krafft, whose excellent experimental work has already been referred to, has extended his observations to a few mono-carboxylic fatty acids, which are connected with the compounds already studied. They correspond to those ketones which were shown to be normal in their atomic volumes.

TABLE VIII.—VOLUMES OF THE FATTY ACIDS.

Compound.	W + 1.	V <sub>m</sub> at m.p. (Krafft).	Δ.	$\frac{V}{W + 1}.$
Lauristic . . C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	77	228.5	35.9 35.8 35.7	2.970
Myristic . . C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	89	264.4		2.970
Palmitic . . C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	101	300.2		2.972
Stearic . . C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	113	335.9		2.972
Mean Value . . . . .	$\left\{ \begin{array}{l} 35.8 \\ 2 \times 17.9 \end{array} \right.$			

The above results indicate that amongst the carboxylic acids the relations  $[O''] = 3[H]$  and  $[O'] = 2H$  hold.

*Volume of  $CO_2$ .*

This may also be deduced in the way shown in the following table :—

TABLE IX.

Fatty Acid.	$V_m$ .	Paraffin.	$V_m$ .	$CO_2$ .
Lauristic . . . $C_{12}H_{24}O_2$	228.5	$C_{11}H_{24}$	201.4	27.1
Myristic . . . $C_{14}H_{28}O_2$	264.4	$C_{13}H_{28}$	237.3	27.1
Palmitic . . . $C_{16}H_{32}O_2$	300.2	$C_{15}H_{32}$	273.2	27.0
Stearic . . . $C_{18}H_{36}O_2$	335.9	$C_{17}H_{36}$	309.0	26.9
Mean Value . . . . .	27.0			

$$9[\text{H}] = 9 \times 2.970 = 26.73.$$

It follows that  $[\text{CO}_2] = 9[\text{H}]$ , and since  $[\text{C}] = 4[\text{H}]$ , then

$$2[\text{O}] = 5[\text{H}] = 15 \times 2.970 = 14.85.$$

*Volume of  $\text{O}_2$ .*

This is also shown to be the case by the following calculations—

	$V_m.$	$\text{O}_2.$
$[\text{C}_{14}\text{H}_{28}\text{O}_2] + 2[\text{H}]$	270.37	
$[\text{C}_{14}\text{H}_{28}]$	255.4	14.97
$[\text{C}_{16}\text{H}_{32}\text{O}_2] + 2[\text{H}]$	306.17	
$[\text{C}_{16}\text{H}_{32}]$	291.2	14.97

The value obtained by difference, is similar to the one calculated. It is approximately equal to  $5[\text{H}]$ . Remembering that  $[\text{O}'] = 3[\text{H}]$ , in the ketones, and that  $[\text{O}'] = 2[\text{H}]$  in the alcohols, we account for the value of O in the group  $-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$  as follows:—

$$[\text{O}'] + [\text{O}] = 3[\text{H}] + 2[\text{H}] = 8.91 + 5.95 = 14.85.$$

*The carboxyl oxygen in the fatty acids thus possesses a similar volume to that of carbonyl oxygen in the ketones, and the remaining oxygen is hydroxylic as in the alcohols.*

The latter may be calculated independently as follows:—

	$V_m.$	$V_m.$
$[\text{C}_{12}\text{H}_{24}\text{O}_2]$ (fatty acid)	228.5	
$[\text{C}_{13}\text{H}_{26}\text{O}]$ (ketone)		240.6
less $[\text{CH}_2]$		- 17.8
		} 222.8

$$\Delta \text{ for } [\text{O}'] = 5.7(2 \times 2.95).$$

Whilst the results are what we may call normal for compounds of about the complexity indicated ( $\text{C}_{16}$ ), simpler compounds are evidently different. The reason has been indicated.

#### *Note on Pelargonic Acid.*

Besides those already noticed, we may remark that Krafft's value for pelargonic acid ( $\text{C}_{18}\text{H}_{17} \cdot \text{COOH}$ ) of melting-point 12.5 is 173.2, or—

$$V_m = 173.2 \text{ observed. } \Sigma_n V_a \text{ 175.2.}$$

This is a number which is larger than the observed value by  $175.2 - 173.2 = 2.0$ , and consequently the latter is depressed to this extent below the normal. If, however, we compare the volume of pelargonic acid with a compound (alcohol) of similar complexity, we observe the following results:—



Alcohol.	$V_m$ .	Acid.	$V_m$ .	
$C_{10}H_{22}O'$	188.3	$C_9H_{18}O'O''$	173.2	
		plus $CH_2$	17.8	
		$\Sigma_n V_a$	191.0	
		$V_m$	191.0	$C_{10}H_{22}O''$

It follows that  $[O''] = 3[H]$  since  $[O'] = 2[H]$ . Then

$$[C_{10}H_{22}O''] - [C_{10}H_{22}O'] = [O''] - [O']$$

$$= 191.0 - 188.3 = 2.7$$

which is a number but little different from the theoretical difference.

$$[O''] - [O] = [H] = 2.97.$$

### Conclusion.

We thus conclude that if at a certain point in a series the volumes of the carbon and hydrogen atoms are similar to their normal values, which have been deduced from a long list of normal paraffins from  $C_{16}H_{34}$  to  $C_{35}H_{72}$ , the values for simpler compounds will fall short, and those for more complex compounds will be in excess of these. This indicates that there is probably a progressive increase in the atomic volumes of, say hydrogen, as measured by the ratio  $V_m/W$  from quite the beginning of a series. This effect is, however, complicated by the alternating factor in alternating series. We shall observe what is possibly a similar result at the boiling-point, and it may be supposed to be due to a want of strict similarity between consecutive members of a series under these conditions. The mode of increase at the melting-point is, however, not quite so clear. In conclusion, we may note that it is probably true, that the molecular volumes of the various compounds in different homologous series, are not quite comparable at the melting-point, and since the melting-points are not related to one another in the same way as the boiling-points of the same series of compounds, we must expect differences in the variations of the volumes of a homologous series at the two points respectively.

As regards the atomic volumes in the carboxylic group, we have found that—

$$\begin{aligned}
 [COOH] &= [C] + [H] + [O'] + [O''] \\
 &= 11.88 + 2.97 + 5.94 + 8.91 \\
 &= 29.7 \text{ (calculated)} \\
 [COOH] &= 30.0 \text{ approx. (by difference).}
 \end{aligned}$$

*Note.*—In order to show how the observed volumes may vary—for reasons unknown at present—Schiff, a very careful and accurate worker, found a value of 333 for stearic acid  $C_{17}H_{35}COOH$ , whilst Krafft, on the other hand, found the volume to be 335.9 for this compound, and in view of the fact that the latter took special care to experiment with pure substances, we must give to his value at least equal weight to that which might be accorded to the other. Moreover, the larger number accords with those obtained for the neighbouring homologous fatty acids by Krafft. This raises the question of why workers of equal reliability should obtain different experimental results, which differences, indeed, seem too large to be ascribed to the effect of impurity, but this can only be settled by very careful and accurate experimental work on substances prepared in several different ways.

### Ring Compounds.

Schiff<sup>10</sup> determined the volumes of a number of aromatic compounds which are possessed of ring structure, in order to find out whether significant volume relations were to be met with, similar to those which Krafft had pointed out for paraffin derivatives at the melting-point. Schiff failed to find such relations, and indeed any significant relations whatsoever.

The reason no doubt is, that the melting-point is a highly constitutive physical property, and if we are to consider the volumes of substances in the liquid state at the melting-point, we must expect large deviations from the values which might be expected from a consideration of their composition alone.

If the compounds are in the liquid state at the melting-point, and we suppose that the structure of liquids does not change in the interval from the boiling to the melting-points, we must suppose that they are subject to the law of coincident states. Under such circumstances we might expect, that a condition of comparison would be found at equal fractions of the boiling-point. The melting-points are not equal fractions of the boiling-point temperatures of the compounds, and thus they do not represent a suitable condition of comparison, at least from the same point of view.

The following investigation shows, that the volumes of compounds are comparable at approximately equal fractions of the boiling-point temperatures :—



TABLE X.

Compound.	m.p. or o°.	b.p.	$1 - \frac{\text{m.p.}}{\text{b.p.}}$ = A.	d m.p.	d b.p.	$\frac{\text{d m.p.}}{\text{d b.p.}} - 1$ = B.	Ratio B/A.
C <sub>6</sub> H <sub>6</sub>	6°	80°	0·210	0·8940	0·8133	0·0980	0·470
C <sub>4</sub> H <sub>4</sub> S	0°	84°	0·236	1·0884	0·9874	0·1023	0·434
C <sub>10</sub> H <sub>8</sub>	79°·2	217°	0·281	0·9777	0·8674	0·1270	0·456
C <sub>10</sub> H <sub>14</sub>	0°	200°	0·423	0·9419	0·7809	0·2062	0·487
C <sub>14</sub> H <sub>10</sub>	100°·5	340°	0·391	1·0630	0·9073	0·1720	0·440
C <sub>5</sub> H <sub>5</sub> N	0°	115°	0·296	1·0033	0·8826	0·1367	0·462
C <sub>9</sub> H <sub>7</sub> N	0°	234°	0·462	1·1081	0·9211	0·2030	0·439
C <sub>10</sub> H <sub>6</sub> · C <sub>2</sub> H <sub>4</sub>	103°	277°	0·316	1·0300	0·9018	0·1422	0·450
Mean . . .							0·455

*Conclusion.*—This table shows, that at equal fractions of the boiling-points the molecular volumes of the compounds are similar although not exactly equal fractions of the volumes at the boiling-points. The nearly constant relation between A and B, indicates that there is a relation between the changes in volume of the molecules, and the changes in temperature, which, so long as the liquid state is maintained, is approximately the same for the ring compounds mentioned and others of similar type. The condition necessary for the volumes at the melting-points to show similar results relatively to each other, as at the boiling-points, is that A should be the same for all, or that the interval between the melting- and boiling-points should, in all cases, be the same fractions of the boiling-point. This condition is not realized, hence the volumes at the melting-points are subject to all the large and preponderant constitutive influences of the melting-points themselves.

The molecular volumes of compounds at the melting-point cannot thus be utilized in the same way as those at the boiling-point.

### General Conclusions.

A number of striking relations have been made out from a study of the open chain hydrocarbons, saturated and unsaturated, and some of the derivatives of the normal paraffins. These investigations, while intrinsically interesting, do not cover sufficient ground to enable us to draw up a list of rules which might be of use in the study of compounds of unknown structure. Moreover the nature of the limitations of the additive rule are not

clearly understood, even in open chain normal compounds. Still less is this so in the case of compounds of more complicated structure, such as ring compounds. This must be ascribed to the highly constitutive nature of the melting point, a feature which would be likely to make the elucidation of the constitutive influences acting on molecular volumes at present a difficult matter. The results obtained, however, show, that in some circumstances, additive relations may be clearly revealed, and what is important to remember, the relative volumes of the atoms are similar to those at the boiling-point. The following table contains a list of the chief results obtained.

TABLE XI.—TABLE OF GENERAL RESULTS.

Atom or Linking.	Value.	Atom or Linking.	Value.
C	11·88 4[H]	— CH : CH <sub>2</sub>   =	— 2·56
H	2·970	— C : CH —   ≡	— 3·20
O'	5·940 2[H]	— C : N —   ≡	— 2·97
O''	8·910 3[H]		
N'''	8·910 3[H]		



## CHAPTER II.

### A STUDY OF THE HYDROCARBONS AT THE BOILING-POINT.

#### The Open-Chain Hydrocarbons.

##### *The Volume of Carbon and Hydrogen.*

THESE atoms are of fundamental importance in a study of the molecular volumes of organic compounds, and as such demand careful consideration. This is especially necessary in view of the fact that Kopp's numbers<sup>11</sup> are unreliable.

We may follow his line of reasoning, by a study of the compounds butane  $C_4H_{10}$  and benzene  $C_6H_6$ , according to his method. Thus:—

$$[C_4H_{10}] = [C_6H_6] = 96.0 \dots (1).$$

It was also shown that

$$[CH_2] = 22.0 \dots (2).$$

From (1) we conclude that  $[C] = 2[H]$ , and applying this to (2), we find that

$$[C] = 11.0 \text{ and } [H] = 5.5.$$

The compounds butane  $C_4H_{10}$  and benzene  $C_6H_6$ , and also those actually studied by Kopp, belong to two entirely different classes of chemical compounds, and are possessed of quite different structures. Butane is an open-chain compound and benzene possesses ring structure. It is thus not necessarily true that similar atoms, are identical in volume, in the two classes of compounds mentioned. This was the assumption Kopp made, and, as we shall see, it was not justifiable.

The most direct way of showing this would be to ascertain the volume of dipropargyl  $C_6H_6$ , a compound which has a structure similar to that of butane and a composition similar to that of benzene. Its molecular volume has not been directly determined, but the probable value can be obtained quite easily, from a study of the available data for the unsaturated hexane derivatives.

TABLE XII.

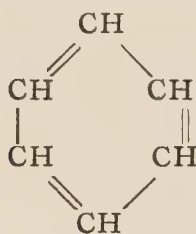
	Compound C <sub>6</sub> .	V <sub>m</sub> .	nH <sub>2</sub> .
Hexane	CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>3</sub>	139.9	
Hexylene	CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH : CH <sub>2</sub>	132.4	7.5
Diallyl	CH <sub>2</sub> : CH . CH <sub>2</sub> . CH <sub>2</sub> . CH : CH <sub>2</sub>	126.1	2 × 6.9
Dipropargyl	CH : C . CH <sub>2</sub> . CH <sub>2</sub> . C : CH	[110.3]	4 × 7.4

The first three compounds have been directly investigated; the fourth value is found by extrapolation, assuming the validity of the summation law.

The volume of dipropargyl:—

CH : C . CH<sub>2</sub> . CH<sub>2</sub> . C : CH is 110.3.

The volume of benzene



is 96.0

$$\Delta = -14.3$$

We conclude, that the volumes of similar atoms, are not the same in the two compounds, nor in the two classes of compounds, and consequently Kopp's assumption is unjustified. It is seen that on passing from open to closed-chain structure, there is a large contraction of - 14.3 which must be accounted for.

The next step, is to show what the actual values of carbon and hydrogen in paraffin and benzene derivatives are.

If we take the same two compounds—butane and benzene—into consideration, and for the moment, suppose that the volume represented by [C<sub>6</sub>H<sub>6</sub>], is that of benzene, but with its atoms similar in volume to those of dipropargyl, then—

$$[C_6H_6] - 4[H] = 96.0.$$

$$\text{But } [C_4H_{10}] = 96.0.$$

$$\text{It follows, that } [C_4H_{10}] = [C_6H_6] - 4[H]$$

$$\text{and thus } [C] = 4[H] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{But } [CH_2] = 22.2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{Therefore } [C] = 14.7 \text{ and } [H] = 3.7.$$

It is interesting to note that the relation [C] = 4[H] is the same as that which was also found to be true at the melting-point.

The values  $[C] = 14.7$  and  $[H] = 3.7$  are the actual atomic volumes of combined carbon and hydrogen at the boiling-point probably in all compounds with open-chain structure. At any rate we must consider them to be the normal values.

The conclusions of contemporary writers were not always the same as those of Kopp, for Lothar Meyer advocated a value of 3.0 for hydrogen, and Loschmidt came very near to anticipating the true values by the numbers  $[C] = 14.0$  and  $[H] = 3.5$ .

The benzene difficulty was got over by assuming that the volume of each of three carbon atoms was equal to 11.0, and that of each of the other three 14.0. The volumes of the hydrogen atoms were given as 3.5.

Reverting to the numbers which are now proposed for combined carbon and hydrogen, we see that they stand in the relation of 4 : 1.

It can be shown that on passing from butane or dipropargyl to benzene the relation already indicated is preserved unimpaired.

Thus, at the *critical point*, the volumes of carbon and hydrogen are

$$[C] = 38.7 \text{ and } [H] = 9.67$$

among the paraffins—values which are as 4 : 1.

For ring compounds, a different result is obtained.

$$\begin{aligned} \text{Benzene } [C_6H_6] &= 256.3 \\ \text{Hexamethylene } [C_6H_{12}] &= 306.7 \\ \hline \Delta \text{ for } 6[H] &= \underline{50.4} = 6 \times 8.40 \\ 6[C] &= 256.3 - 50.4 = 205.9 \\ \text{and } [C] &= 34.3 \text{ or } 4 \times 8.57, \\ [H] &= 8.40. \end{aligned}$$

These values are also approximately in the relation of 4 : 1. By assuming this relation to be true, and dividing the critical volumes of benzene and hexamethylene by the respective valency numbers, we obtain nearly constant values for  $V_m/W$ , which values represent the volume of hydrogen.

	$V_m^c$	W.	$V_m^c/W$
Benzene $C_6H_6$	256.3	30	8.54
Hexamethylene $C_6H_{12}$	306.7	36	8.52

The 4 : 1 rule may be shown to be true, not only at the boiling and critical points, but also at all equally reduced pressures.



We conclude from this, that on passing from the aliphatic to the aromatic class of compounds, the volumes of the carbon and hydrogen atoms undergo a contraction, but in such a way as to preserve the characteristic numerical relation unimpaired. The total contraction for benzene and the other ring compounds is equal to the sum of the contractions of all the atoms in the nuclei.

TABLE XIII.—DIRECT INVESTIGATION OF THE ATOMIC VOLUMES OF CARBON AND HYDROGEN. See Le Bas (*loc. cit.*) and *ref.*<sup>12</sup>

Substance.	$V_m$ .	$\Delta$ for $\text{CH}_2$ .
$\text{C}_5\text{H}_{12}$	117.8	22.1
$\text{C}_6\text{H}_{14}$	139.9	

$$2[\text{H}] = [\text{C}_5\text{H}_{12}] - 5[\text{CH}_2] = 117.8 - 5 \times 22.1 = 7.3 \quad (2 \times 3.65)$$

$$[\text{C}] = 22.1 - 7.3 = 14.8 \quad (4 \times 3.70).$$

The above results are thus in favour of the average atomic volumes already given— $[\text{H}] = 3.70$  and  $[\text{C}] = 14.8$ , and the evidence seems to be indisputable. The result of such evidence is to completely invalidate the original numbers of Kopp.

Those which have just been obtained, are, however, also supported by a comparison of the volumes of certain normal paraffins, olefins, diolefins, etc.

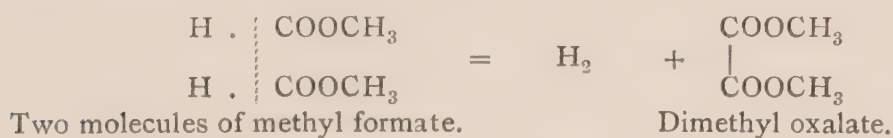
TABLE XIV.—THE ATOMIC VOLUME OF HYDROGEN.

Substance.	$V_m$ .	$n\text{H}_2$ .	$V_m$ .	Olefin.
$\text{C}_5\text{H}_{12}$	117.8	7.7	110.1	$\text{C}_5\text{H}_{10}$
—	—	$2 \times 6.7$	104.5	$\text{C}_5\text{H}_8$
$\text{C}_6\text{H}_{14}$	139.9	7.5	132.4	$\text{C}_6\text{H}_{12}$
—	—	$2 \times 6.9$	126.1	$\text{C}_6\text{H}_{10}$
$\text{C}_3\text{H}_7(\text{OH})$	81.5	7.3	74.2	$\text{C}_3\text{H}_5(\text{OH})$
$\text{C}_3\text{H}_7\text{Cl}$	91.7	7.3	84.4	$\text{C}_3\text{H}_5\text{Cl}$
$\text{N}(\text{C}_3\text{H}_7)_3$	222.4	$3 \times 7.2$	200.7	$\text{N}(\text{C}_3\text{H}_5)_3$
Mean value of $[\text{H}]_2 = 7.15$				

A similar result is obtained from a consideration of the volumes of ethyl benzene, and its unsaturated derivatives.

Compound.	$V_m$ .	$\Delta$ for $n\text{H}_2$ .
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_3$	139.3	7.8
$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$	131.5	
$\text{C}_6\text{H}_5 \cdot \text{C} : \text{CH}$	126.2	$2 \times 6.6$

The above compounds are for the most part unsaturated, but similar results can be obtained from a consideration of saturated ones. Thus—



$$2[\text{H}] = 2[\text{H} \cdot \text{COOCH}_3] - [(\text{COOCH}_3)_2] = 125.0 - 117.4 = 7.6.$$

It follows from the above calculations that the average volume of combined hydrogen in organic compounds is—

$$[\text{H}] = 3.70.$$

TABLE XV.—THE ATOMIC VOLUME OF CARBON.

Substance.	$V_m$ .	$\Delta$ for Carbon.	$V_m$ .	Olefin.
$\text{C}_4\text{H}_{10}$	96.0	14.1	110.1	$\text{C}_5\text{H}_{10}$
$\text{C}_5\text{H}_{12}$	117.8	14.6	132.4	$\text{C}_6\text{H}_{12}$
$\text{C}_6\text{H}_{14}$	139.9	14.9	154.8	$\text{C}_7\text{H}_{14}$
$\text{C}_7\text{H}_{16}$	162.6	15.0	177.6	$\text{C}_8\text{H}_{16}$
Mean value of carbon $[\text{C}] = 14.6$				

The average volume of carbon, taking all the data into consideration, is—

$$[\text{C}] = 14.8.$$

The volumes of combined carbon and hydrogen given above, are average ones only, and, as such, are of no special significance. They are, however, useful for purposes of calculation.

If we except liquid hydrogen itself, and perhaps methane, the combined volume varies within the comparatively narrow limits of 3-4, even including compounds of widely different structure.

*Note on the Effect of Unsaturation at the Boiling-point.*—A note is required on the result which has been obtained for unsaturation. It is seen that the values for corresponding members of the  $n$  paraffin, olefin and acetylene series are simply dependent on their composition. *There is thus no special effect due to unsaturation at the boiling point.* The evidence for this conclusion is so strong that it is scarcely open to question.

Very different results have previously been obtained by different observers. Buff<sup>13</sup>, in 1865, sought to show that carbon possesses greater volume in unsaturated than in saturated compounds. This was apparently confirmed by Schiff,<sup>14</sup> who calculated that the increase for single unsaturation, was 4.0 units, approximately. Thus—

	$V_m.$
Amylene $C_5H_{10}$	110.0
Pentane $C_5H_{12}$	117.2
	<hr/>
$\Delta$	= 7.2

$$\begin{aligned} \text{Then if } H_2 &= 2 \times 2.55 \\ | = | &= 110.0 - 7.2 = + 3.8. \end{aligned}$$

Lossen<sup>15</sup> thought that this increase was due to the hydrogen rather than the carbon.

These results are evidently due to the particular atomic volumes of hydrogen and carbon chosen.

If we grant the validity of the new numbers, the observation, that unsaturation is responsible for no special effect, follows as a matter of course.

*The Influence of Complexity on Molecular Volumes, especially that connected with the Influence of the Homologous Increment.*

It has been repeatedly stated that the additive rule is not quite followed in molecular volumes. This was first shown by Gartenmeister,<sup>16</sup> Döbriner,<sup>17</sup> Schiff,<sup>18</sup> Pinette,<sup>19</sup> Zander,<sup>20</sup> and others, from the study of the compounds of various homologous series, that is, compounds which differ in constitution by the group methylene ( $CH_2$ ). The series in question are those of the ethereal salts of the fatty acids, the ethers, the alkyl iodides, etc.

More recently, Young<sup>21</sup> has shown, that, under a variety of conditions, the normal paraffin series of compounds, always differ from term to term when the group  $CH_2$  is added. Thus, under no circumstances, is the additive rule exactly realized.

The differences in volume between two successive terms of a series, have, however, been shown to give unreliable information regarding the extent to which the additive rule is departed from. The accompanying table shows this.



TABLE XVI.—THE VOLUMES OF THE *n* PARAFFINS AT THE BOILING AND CRITICAL POINTS.

Substance.	W.	$V_m$ at the boiling- point.	$\Delta$ .	$V_m/W$ .	$V_m^c$ .	$\Delta$ .	$\frac{V_m^c}{W}$ .
<i>n</i> Butane $C_4H_{10}$	26	96.0	21.8	3.693	251.0	58.3	9.654
<i>n</i> Pentane $C_5H_{12}$	32	117.8	22.13	3.681	309.3	56.8	9.666
<i>n</i> Hexane $C_6H_{14}$	38	139.93	22.63	3.682	366.1	60.2	9.634
<i>n</i> Heptane $C_7H_{16}$	44	162.56		3.693	426.3		9.689

If we take into consideration the fact that in the aldehydes the volume of oxygen is equal to twice that of hydrogen, and that, so far as a comparison can be made, the members of the two series possess almost identical volumes, we do not perhaps commit any very serious error, if we suppose that the volumes of the simplest paraffins, are similar to those of the aldehydes, which have been investigated.

TABLE XVII.—THE VOLUMES OF THE NORMAL PARAFFIN SERIES.<sup>22</sup>

Substance.	W.	$V_m$ .	$V_m/W$ .
$CH_4$	8	38.5	4.812
$C_2H_6$	14	56.7	4.050
$C_3H_8$	20	74.6	3.730
$C_4H_{10}$	26	96.0	3.693
$C_5H_{12}$	32	117.8	3.681
$C_6H_{14}$	38	139.93	3.682
$C_7H_{16}$	44	162.56	3.695
$C_8H_{18}$	50	186.26	3.725

The curve shown on next page is similar to those obtained for many series and indicates the variations in the volume of combined hydrogen in the series. It consists of three parts:—

(a) *A descending arm*: This shows that the volumes of hydrogen diminish rapidly from compound to compound.

(b) *A minimum*: The volumes of hydrogen are a minimum at this point. For a limited range of complexity the atomic volumes do not differ much. It is to this circumstance that the approximate additive relations which have been noted, are due.

(c) *An ascending arm*: The values of  $V/W$  increase, possibly in a rectilinear way.

The influences which contribute to the above result, are not quite clear, but we are probably correct in supposing that several are operative. The following explanation seems to be at least plausible. We suppose, that, at any rate, the following two influences are probably important: (a) the influence of the element carbon with its enormous power of self affinity; (b) and the effect of the volatile hydrogen with its large molecular volume. These

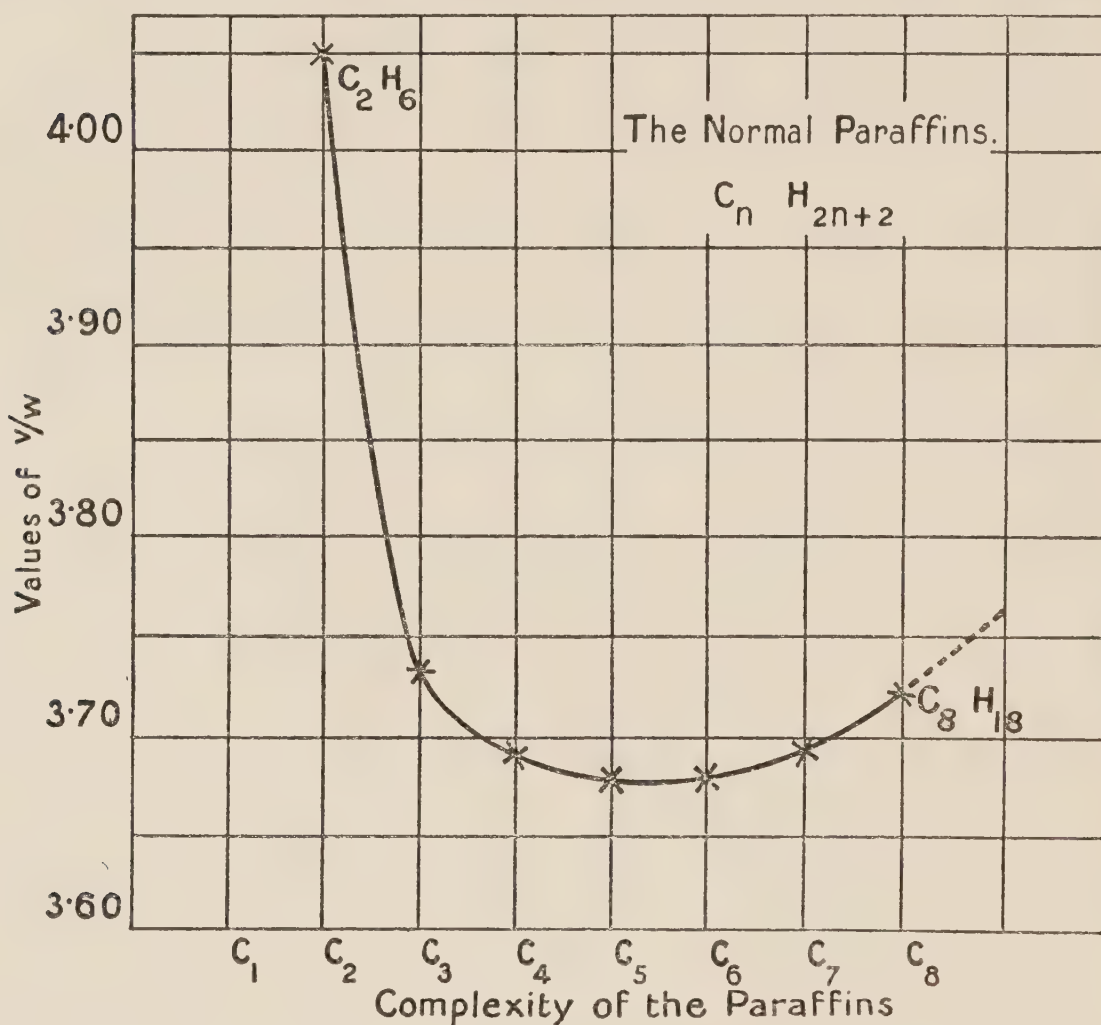


FIG. 1.

characteristics are not lost in combination. It follows, that the volume of methane, might be expected to be relatively large, owing to the large proportion of hydrogen atoms present in the molecule, compared with the number of carbon atoms. As methylene groups ( $CH_2$ ) are added, the proportion of carbon increases, and thus there is a very considerable diminution in the values of  $V_m/W$ . The reason for the ultimate increase in the value  $V_m/W$  is not quite so clear. This possibly is owing to a gradually changing relation of the volumes to the boiling-points, which also involves the magnitude of the internal pressures due to the

intramolecular forces. Thus in general terms, we suppose that the intramolecular and consequently the intermolecular forces are different among the different compounds of a homologous series, so that the molecules are freed at temperatures which do not preserve the necessary volume relationships which make the compounds completely homologous. The extent by which they differ indicates the constitutive differences between them. Young attributes these variations to constitutive causes.

*The Branching of the Hydrocarbon Chain.*

This is the only constitutive influence likely to affect the volumes of the open-chain hydrocarbons, since unsaturation does not cause any special effect. The data are, however, very meagre, so that the conclusions have not that proved generality which is desirable.

The iso structure seems to cause a definite lowering of the boiling-point (8-9 degrees), and a definite contraction (0.50).

TABLE XVIII.—CONTRACTION FOR THE ISO GROUP.

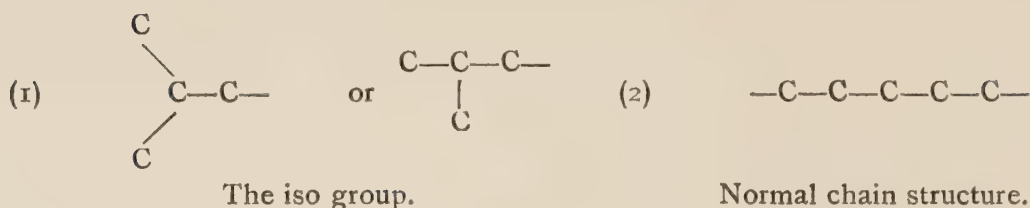
Normal Compound.	$V_m$ .	Iso Group.	$V_m$ .	Iso Compound.
<i>n</i> Pentane $C_5H_{12}$	117.8	-0.40	117.4	$(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_3$
<i>n</i> Hexane $C_6H_{14}$	139.9	-0.50	139.4	$(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_3$
<i>n</i> Heptane $C_7H_{16}$	162.9	-0.60	162.3	$(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$
<i>n</i> Octane $C_8H_{18}$	186.6	-0.90 $\times 2$	185.2	$(CH_3)_2 \cdot CH \cdot (CH_2)_2 \cdot CH_3 \cdot (CH_3)_2$
Valerylène $C_5H_8$	104.2	-0.30	103.9	Isoprene
$\Delta = -0.53$				

The contractions due to the presence of the iso group, seem to increase with complexity, and the average value is about

(Iso group) 0.50.

The observed contraction, which is characteristic of compounds with the *iso* group, is no doubt associated with a greater concentration of matter at the point at which this group is situated, than at other points in the molecules. This is shown by the following scheme—





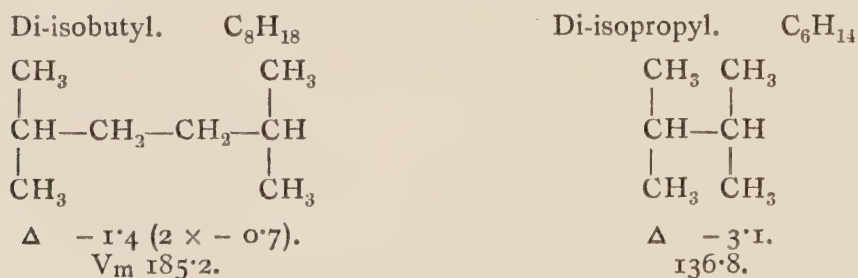
The contractions which have just been indicated, illustrate that great capacity for self-affinity which characterizes carbon, and which is most effective when the atoms are most concentrated. It is possible that the large contractions which distinguish ring structure, may be due to this cause. This more compact arrangement, affects not only the carbon, but the hydrogen atoms also.

Naumann<sup>23</sup> in 1874 stated the following rule for the boiling-points of the paraffins and other open-chain hydrocarbons: "*The more nearly the grouping of the atoms in an isomeric paraffin deviates from the rectilinear or chain type, and approaches the spherical type, the lower is the boiling-point*".

A similar rule, moreover, may perhaps apply to the molecular volume, that is, so far as observation goes, and the rule may have as great generality for volumes as for boiling-points, provided we limit it to the various hydrocarbon series.

### *The Interaction between Methyl Groups.*

The average value of the contraction for an iso group is  $-0.5$ , and one of about twice the magnitude may be deduced from the volume of di-isobutyl which contains two iso groups. For di-isopropyl, where the iso groups are nearer to each other, a much larger contraction is noticed.

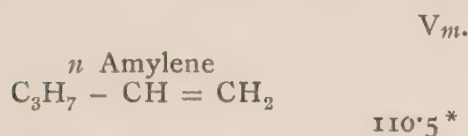


The magnitude of  $\Delta$  in di-isobutyl is equal to the contraction caused by two iso groups acting independently, but this double value is augmented in di-isopropyl, owing to the closer approximation, and consequently probable interaction of these groups. The augmentation in question, is—

$$-(3.1 - 1.4) = -1.7,$$

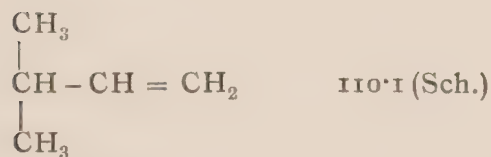
The real cause of the above contraction is considered to be due to the interaction of  $\text{CH}_3$  groups attached to different carbon atoms. This is evident from the diminished boiling points.

If we consider a compound in which an iso group and an ethenoid linkage are close to one another, we shall notice a disturbance in the total value of the constitutive effect.



\* [This value has been calculated by subtracting 7.3 from the molecular volume of pentane  $V_m = 117.8$ .]

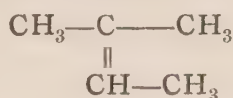
$\alpha$  Amylene  $\Delta = 0.40$  This is about equal to one iso group.



$\beta$  Amylene  $\Delta = 2.40$



Reasons are given later on for supposing that the above contraction is due to the interaction of two  $\text{CH}_3$  groups. This necessitates a modification of the above formula, thus—



Other compounds of this type are studied later on. The rule is that *when two methyl groups (or four) are attached to neighbouring carbon atoms there are contractions due probably to interaction between these groups.*

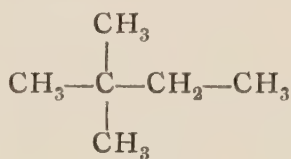
In the foregoing account, we have dealt entirely with the influence of the iso group, but of course, a hydrocarbon chain may be divided up in different ways.

#### *The Influence of the Tertiary Grouping on Volume.*

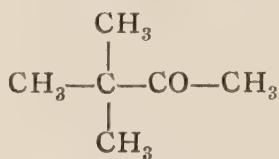
Doubtless the grouping  $(\text{CH}_3)_3\text{C} -$  would show an increased contraction, as compared with an iso grouping, but actual data are lacking for the hydrocarbons. The volume of pinakolin  $(\text{CH}_3)_3 \cdot \text{C} \cdot \text{CO} \cdot \text{CH}_3$  is 138.6, and if the volume of  $\text{O}'$  be equal

to  $2H$ , as is usual in such compounds, then the volume is equal to that of trimethylethyl methane  $(CH_3)_3 \cdot C-CH_2-CH_3$ .

Trimethyl methane.

 $V_m$  138·6.

Pinakolin.



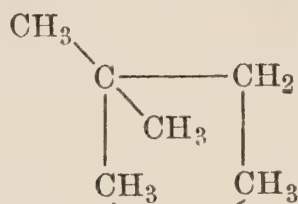
138·6

The volume of the hydrocarbon, is thus, about 138·6, a value which is less than that of normal pentane by  $139·9 - 138·6 = 1·3$ . This value is,—

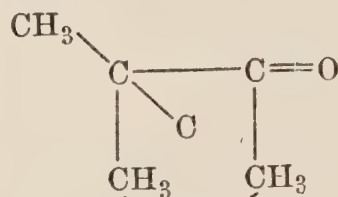
$$\Delta = -1·3 = -0·65 \times 2,$$

or the contraction due to this tertiary group is twice that for an iso group.

In some of the compounds at any rate, the contraction may be due, in part at least, to an interaction of groups attached to different carbon atoms. This is seen to be possible if we give to trimethyl methane and pinakolin the following configurations—



Trimethyl methane.



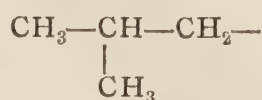
Pinakolin.

This possibility is lost sight of in the plane formulæ, but the solid models or diagrams to represent them, would show this.

This fact may be explained as follows:—

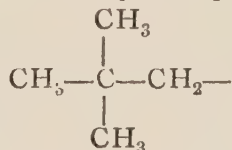
If we suppose, that, in the iso and tertiary groups, one  $CH_3$  group is continuous with the main chain, then the other  $CH_3$  group in the iso arrangement, and the other two  $CH_3$  groups in the tertiary, respectively occupy the  $\beta$  positions, as shown in the subjoined schemes.

Iso Group.



$$\Delta = -0·50$$

Tertiary Group.



$$\Delta = -1·3 = 2 \times -0·65$$

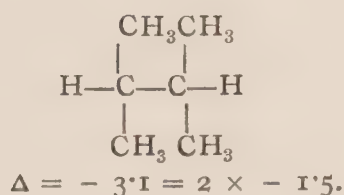
The  $CH_3$  groups, in effect, substitute hydrogen atoms from the  $\beta$  position, like chlorine or other atoms would, and consequently the  $CH_3$  groups occupy similar positions to the latter in the



molecule. It consequently represents two propane residues, joined together by their middle carbon atoms.

These formulæ are similar to those upon which the "Geneva Commission" has based its system of nomenclature, and the formulæ suggested by it would seem to have theoretical justification.

The formula for di-isopropyl, taking into consideration the contraction is



### Unsaturated Compounds.

In studying the hydrocarbons, it will be of great advantage to consider the branching of the chain as equivalent to substitutions of the methyl group for hydrogen. Moreover, if more than one substitution has taken place, the distribution may be

- (a) Unsymmetrical  $\text{CHX}_2 \cdot \text{CH}_3$   
 $\text{CX}_2 : \text{CH}_2$   
 (b) Symmetrical  $\text{CH}_2\text{X} \cdot \text{CH}_2\text{X}$   
 $\text{CHX} : \text{CHX}$   
 $\text{CX}_2 : \text{CX}_2$

These features will affect both the molecular volumes and the boiling-points of the compounds.

The following rules have been made out:—

#### *Unsymmetrical Distribution.*

CH <sub>3</sub> group	(CH <sub>3</sub> ) <sub>2</sub> CH —	ΔV — 0·5	b.p. — 8·0
	(CH <sub>3</sub> ) <sub>3</sub> C —	ΔV — 1·0	— 28·0
Cl	Cl <sub>2</sub> CH —		gradually diminishing differ-
	Cl <sub>3</sub> C —	ΔV + 1·5	ences for Cl—H, showing
	Cl <sub>4</sub> C	ΔV + 3·0	depression with continued substitution.

#### *Symmetrical Distribution.*

CH <sub>3</sub> group	— C(CH <sub>3</sub> ) <sub>2</sub> · C(CH <sub>3</sub> ) <sub>2</sub> —	ΔV — 1·5 to — 3·1	b.p. + 5·0
Cl	— CHCl · CHCl —	— 3·1	+ 23·6
	— CHBr · CHBr —	— 3·1	+ 20·3

The following olefins are normal, or nearly so:—

Mono-Olefins.		$V_m$	V of sat. compd.	less $n \times 7.4$ or $\Sigma n V_a$
$\beta$ Amylene	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_3$	110.1	117.8	110.4
$\alpha$ Hexylene	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2$	132.4	139.9	132.5
$\alpha$ Heptylene	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2$	154.8	162.6	155.2
$\alpha$ Octylene	$\text{CH}_3 \cdot (\text{CH}_2)_5 \cdot \text{CH} : \text{CH}_2$	177.6	—	176.8
Di-Olefins.				
Isoprene	$\text{CH}_2 : \text{CH} \cdot \text{C}(\text{CH}_3) : \text{CH}_2$	103.6	—	—
Diallyl	$\text{CH}_2 : \text{CH} \cdot (\text{CH}_2)_2 \cdot \text{CH} : \text{CH}_2$	125.1	139.9	125.1
Aromatic unsaturated compound.				
Styrolene	$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$	131.4	139.3	131.9

The following olefins are abnormal :—

Pseudo butylene (dimethyl ethylene) symmetrical compound.

$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_3$  b.p. + 1°

b.p. of  $\alpha$  compound — 5°

For  $\text{CH}_3$  groups in  $\alpha \beta$  pos. + 6

Calculated b.p. + 1°

valerylene —  $d_{13}$  0.653 (Chem. kal.)  $\Delta = 0.00075$ .

$d_1$  0.653 +  $12 \times 0.00075 = 0.644$   $V_m$  86.9.

$\Sigma n V_a = 96.0 - 7.4 = 88.6$ .

$\Delta = V_m - \Sigma n V_a = 86.9 - 88.6 = -1.7$ .

There is thus an increase in boiling-point for symmetrical distribution (6°) and a contraction of — 1.7.

Trimethyl ethylene  $(\text{CH}_3)_2 \cdot \text{C} : \text{CH}(\text{CH}_3)$

b.p. 36°  $V_m$  108.1 (Thorpe).

b.p. of  $\text{C}_5\text{H}_{11}$  ||  $\beta$  amylene 39°

corr. for iso group — 8

—

31

for  $\alpha \beta$  const. + 5

—

calculated b.p. 36

observed 36

compare

$\text{C}(\text{CH}_3)_2 : \text{CH}(\text{CH}_3)$

$\Delta = -2.0$

with

$\text{CCl}_2 : \text{CHCl}$

$\Delta = -1.5$

for contractions

Since the volume of

$\alpha$  or  $\beta$  amylene is  $V_m$  110.1

and for trimethyl ethylene 108.1

$\Delta = -2.0$

The contraction — 2.0 is connected with the symmetrical distribution of the methyl groups.

Di-isopropyl.

$\text{CH}(\text{CH}_3)_2 \cdot \text{CH}(\text{CH}_3)_2$

b.p. 58.0

b.p.  $n \text{ C}_6\text{H}_{14}$  71°

less two iso groups — 18 ( $2 \times 9$ )

—

calculated 53

observed 58

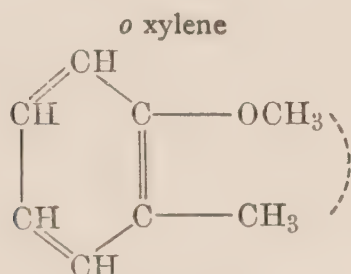
$\Delta = +5$

There is thus an increase above the expected value. This result is no doubt due to the interaction of neighbouring iso groups. Also—

$$\begin{array}{r} V_m \quad 136.8 \\ \Sigma nV_a \quad 139.9 \\ \hline \Delta = \quad \underline{\underline{-3.1}} \end{array}$$

The contraction for this compound is thus  $-3.1$  below the normal.

The following example from among the aromatic compounds will help us to solve the problem of the constitution of these compounds.



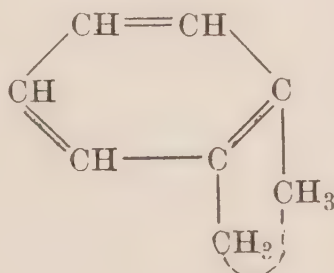
	b.p.	$V_m$
<i>o</i> xylene	141.9	137.9
<i>p</i> xylene	138.9	140.2
$\Delta$	<u>+3.9</u>	<u>-2.3</u>

There is thus an increase in the boiling-point of  $+3.9$ , and a contraction of  $-2.3$  owing to the approximation of the methyl groups.

A further study of the tri- and tetra-methyl benzenes shows results which are similar.

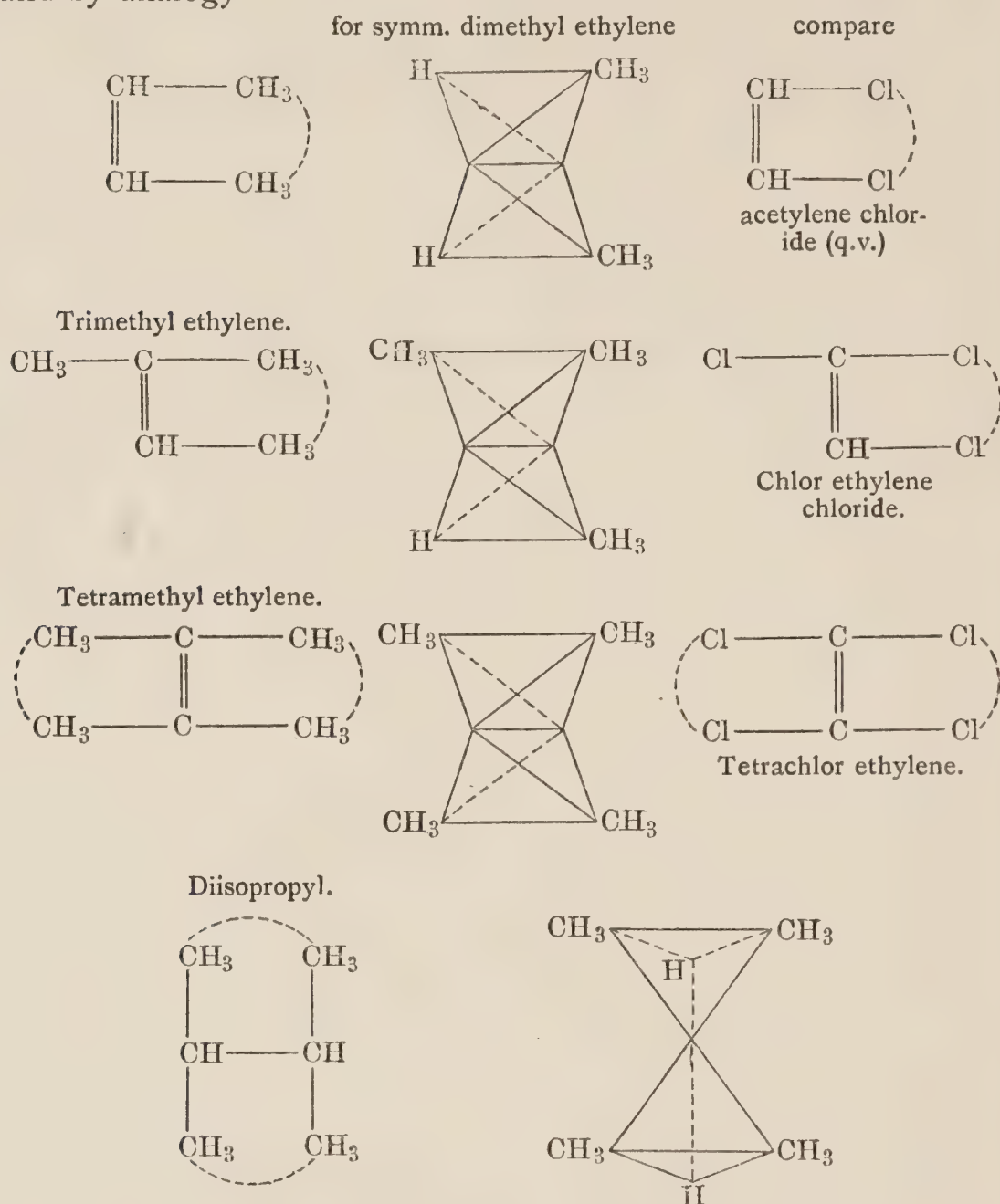
	$\Delta V$	b.p.
Sym. dimethyl ethylene $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_3$	- 1.7	+ 6°
Trimethyl ethylene $(\text{CH}_3)_2\text{C} : \text{C}(\text{CH}_3)$	- 2.0	+ 5°
Tetramethyl ethylene $(\text{CH}_3)_2\text{C} : \text{C}(\text{CH}_3)_2$	- 4.6	+ 14°
Diisopropyl $(\text{CH}_3)_2\text{CH} \cdot \text{CH}(\text{CH}_3)_2$	- 3.1	+ 5°
<i>o</i> Xylene $\text{C}_6\text{H}_4(\text{CH}_3)_2$	- 2.3	+ 3.9 from <i>p</i> xylene + 5.4 from ethyl benzene

The formula for *o* xylene would be





and by analogy



In all these cases where there is an augmentation of the boiling-point and a diminution of the volume, there is spatial proximity of the  $\text{CH}_3$  groups. We therefore conclude that the effect is due to an interaction of the groups.

A convincing piece of evidence is found in an examination of the volumes of the di- and polyhalogen derivatives of the paraffins.

The chlorine atom in propyl chloride (terminal) has a volume of 21.5 and in isopropyl chloride (central) a volume of 24.3. The sum of the volumes of these two chlorine atoms is 45.8.

Propylene chloride which has one chlorine atom in the  $\alpha$

position and one in the  $\beta$  position has such a volume that the sum of the two chlorine atoms is apparently 41.6. There is thus a considerable diminution in volume caused by the presence of the two chlorine atoms in the same molecule, one in the  $\alpha$  and one in the  $\beta$  position.

### Closed-Chain Hydrocarbons.

#### *Aromatic Hydrocarbons and Ring Structure.*

There is a constitutive effect in these compounds which is due to ring structure, as already shown. Without going more fully into the question of the cause of ring structure at present, we simply calculate the values of  $\Sigma nV_a$ , and express this correction as a negative difference.

TABLE XIX.—RING HYDROCARBONS.

Substance.	$V_m$ .	$\Sigma nV_a$ .	$\Delta$ ,
Diamylene . . . $C_{10}H_{20}$	211.7	220.3	— 8.6
Benzene . . . $C_6H_6$	96.0	111.0	— 15.0
Toluene . . . $C_6H_5 \cdot CH_3$	118.3	133.2	— 15.1
<i>p</i> Xylene . . . $C_6H_4(CH_3)_2$	140.5	155.4	— 14.9
Ethyl benzene . . . $C_6H_5C_2H_5$	139.5	—	— 15.9
Mesitylene . . . $C_6H_3(CH_3)_3$	162.8	177.6	— 14.8
Propyl benzene . . . $C_6H_5C_3H_7$	162.2	—	— 15.4
Cymene . . . $C_6H_4(CH_3)C_3H_7$	184.9	199.8	— 14.9
Hexamethylene . . . $C_6H_{12}$	116.3	133.2	— 16.9
Hexahydrotoluene . . . $C_6H_{11}CH_3$	141.8	155.4	— 13.6
Hexahydroxylene . . . $C_6H_{10}(CH_3)_2$	164.3	177.6	— 13.3
Naphthalene . . . $C_{10}H_8$	147.2	177.6	— 30.4
Naphthyl hydride . . . $C_{10}H_{14}$	171.2	200.0	— 28.8
Anthracene . . . $C_{14}H_{10}$	195.5	244.2	— 48.7

### Simple Rings.

#### *Homologues of Benzene.*

Benzene $C_6H_6$	$V_m$ 96.0	H 3.2.
	$V_m$ .	
Toluene $C_7H_8$	118.25 (Schiff)	
$C_6H_5 - CH_3$		
$C_6H_5 -$	92.8	
	—	

	$\Delta$ for $\text{CH}_3$	25.45	$[\text{CH}_3] = 25.45.$
<i>p</i> xylene $\text{C}_8\text{H}_{10}$	$\text{C}_6\text{H}_4 (\text{CH}_3)_2$	140.5 (S.)	
	$\text{C}_6\text{H}_4$	89.6	
	$\Delta$ for $2\text{CH}_3$	50.9	$[\text{CH}_3] = 25.45.$
Ethyl benzene	$\text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_5$	139.28 (S.)	
		$[\text{C}_2\text{H}_5] = 47.48$	
		In paraffins	48.0
		$\Delta$	- 0.5.
Mesitylene $\text{C}_9\text{H}_{12}$	$\text{C}_6\text{H}_3 (\text{CH}_3)_3$	162.67 (S.)	
	$\text{C}_6\text{H}_3$	86.4	
	$\Delta$ for $3\text{CH}_3$	76.27	$[\text{CH}_3] = 25.42$
			In paraffins 26.0 and larger
			$\Delta$ - 0.6.
Propyl benzene	$\text{C}_6\text{H}_5 \cdot \text{C}_3\text{H}_7$	162.16 (S.)	
		$[\text{C}_3\text{H}_7] = 69.36$	
		In paraffins	70.0
		$\Delta$	- 0.6.

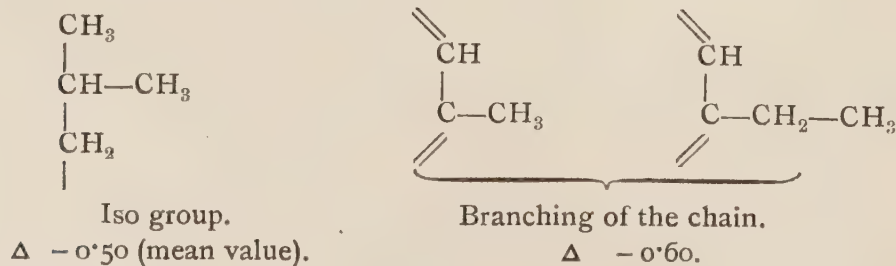
The volume of  $\text{CH}_3$  is evidently the same in all these compounds, and is slightly less than in those which have an open-chain structure.

$$\begin{array}{rcl}
 [\text{CH}_3] \text{ (in the paraffins)} & = & 25.9 \\
 [\text{CH}_3] \text{ (in aromatic side chains)} & = & 25.5 \\
 \hline
 \Delta & = & \underline{\underline{-0.4}}
 \end{array}$$

The groups  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$  also show a contraction as compared with similar residues in open-chain compounds. The contraction is - 0.6.

This is probably to be accounted for in a similar way to that for the iso group.

Thus we have—



The diagrams show a great similarity between the modes of arrangement of the atoms in the two classes of compounds.



The principle is not affected if we suppose that the paraffin residues are directed along a line which cuts the rings at right angles, or nearly so. This is equivalent to branching.

The volume of cymene may thus be synthesized:—

Cymene  $C_3H_7 \cdot C_6H_4 \cdot CH_3$

$C_6H_4$	89.6
$CH_3$	25.45
$C_3H_7$	69.36
$\Sigma nV_a$	184.41
$V_m$	184.88

*p* methyl ethyl benzene.

$C_6H_4(CH_3)(C_2H_5)$

$C_6H_4$	89.6
$CH_3$	25.45
$C_2H_5$	47.48
$\Sigma nV_a$	162.53
$V_m$	162.32

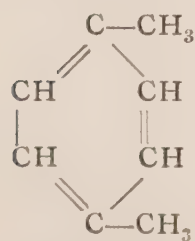
There are thus slight differences both + and – in the results from which it would appear that small quantities of impurity might have been present in Schiff's material. For example small quantities of the ortho modification in *p* methyl ethyl benzene would account for the result. These compounds are notoriously difficult to completely purify.

### *The Effect of Self-Affinity between the Side-chains of Aromatic Compounds.*

It has been shown that in the open-chain hydrocarbons self-affinity is manifested by contiguous paraffinoid groups.

The same effect is well shown by the various aromatic compounds which possess two contiguous hydrocarbon side chains. The data are due to Pinette (*loc. cit.*).

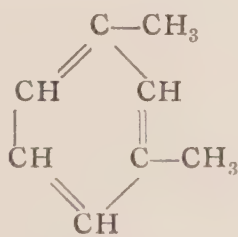
The xylenes  $C_8H_{10}$ .



para (1 : 4)

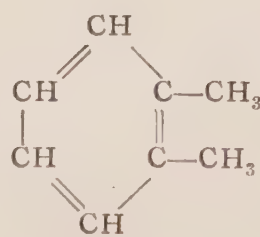
$V_m$   
 $\Delta$

140.25



meta (1 : 3)

140.00



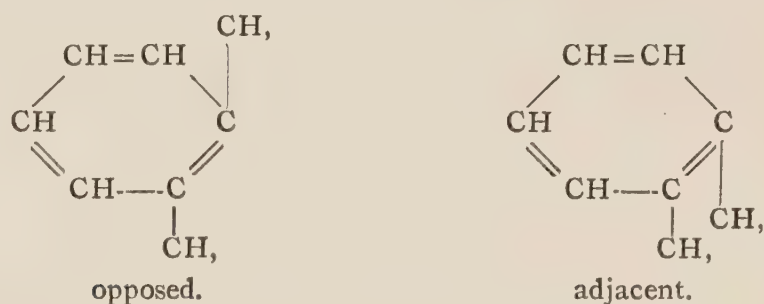
ortho (1 : 2)

137.95

Difference between o and p  $\Delta = - 2.3$

3 \*

Strictly speaking two possible geometrical isomers of ortho xylene should be accounted for, as perhaps also for the others. They are:—



These isomers are constructed according to the well-known fumaroid and malenoid types. If we examine the data carefully we shall find that they agree with those which might be expected to apply to the two forms.

TABLE XX.—THE VOLUMES OF THE XYLENES.

	Schiff. <sup>24</sup>		Pinette. <sup>25</sup>		Neubeck. <sup>26</sup>	
	<i>V<sub>m</sub></i> .	b.p.	<i>V<sub>m</sub></i> .	b.p.	<i>V<sub>m</sub></i> .	b.p.
Para . . .	140·5	136·5	140·25	138·0	140·77	138·4
Meta . . .	140·2	139·2	140·1	138·9	140·1	139·1
Ortho . . .	140·2	141·1	137·9	141·9	138·2	141·1
Δ between <i>o</i> and <i>p</i>	—0·3		—2·3		—2·07	

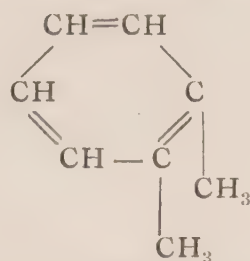
It is observable that, as we pass from the para to the ortho compound, there is, on the whole, an increase in the boiling-point, and diminution in the volume. Comparing the values given by the different observers, we find between the para and the meta modifications, differences which are of a minor character.

It is to be observed in regard to the ortho compound, that the boiling-points are similar, whilst the differences between the volumes obtained by different observers, are far too great to be ascribed to accidental causes. Pinette's value is supported by that of Neubeck. Schiff, on the other hand, was a chemist of well-founded reputation for care and accuracy, so that his value is at least entitled to equal weight.

It thus seems that the two sets of values refer to different forms of the same compound. Moreover, the lower values differ from that which might be expected by an amount equal to

about 2.5. This is a normal feature of ortho compounds, if we consider the data available, and has been accounted for by supposing that there is an interaction between the groups owing to residual affinity. The lower value would thus correspond to the

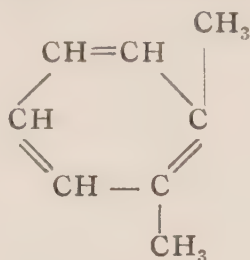
“Adjacent” orthoxylene.



$$V_m = 138.2.$$

Schiff's larger volume is similar to that for paraxylene, thus showing that the groups are independent and unable to interact. This therefore corresponds to the

“Opposed” orthoxylene.



$$V_m = 140.2.$$

On looking at the two formulæ we see that there is every reason to expect two forms.

A study of other derivatives of benzene shows similar peculiarities to those already noticed.

In the first place we must note the characteristics of “adjacent” and “opposed” varieties of a compound. (See App. II.)

The esters of maleic and fumaric acid.

	Maleate.	$\Delta$	Fumarate.
Methyl.	b.p. 208°	+ 16.0	192°
Ethyl.	225	+ 7.0	218
	Maleic.		Fumaric.
	CH = CH		COOCH <sub>3</sub>
	COOCH <sub>3</sub> COOCH <sub>3</sub>		CH = CH
			COOCH <sub>3</sub>

Similar observations are made in the case of benzene derivatives. The ortho variety is usually some degrees higher in boiling-point than the para, and this we believe to be due to a conjunction of groups.



	<i>p</i> xylene	<i>m</i> xylene	<i>o</i> xylene
b.p.	138°	139°	142°
	+ 4°		
	Dichlorides.		
	para	meta	ortho
b.p.	172°	172°	179°
	+ 7°		
	Dibromides.		
	para	meta	ortho
b.p.	219°	219°	224°
	+ 5°		

The above and other data show that the meta is similar to the para, but that the ortho is some degrees higher.

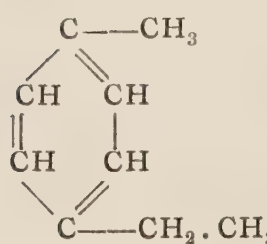
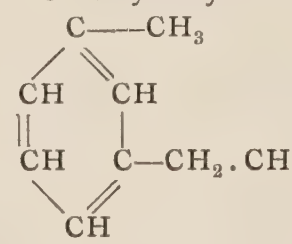
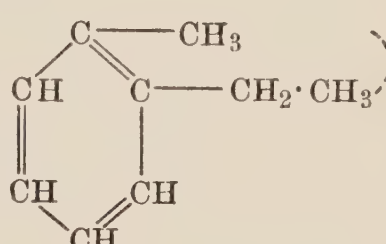
So we have shown that there is a difference in volume of about  $-2.0$ .

We, however, find apparent exceptions to the above rule.

	The chlor toluenes.				
	para		meta		ortho
b.p.	163°	- 13.0	150	+ 6°	156°
	- 7°				
	The brom toluenes.				
	para		meta		ortho
b.p.	184°		183°		181°
	- 3°				

These anomalous results, where not due to association, may very well be the result of stereo isomerism.

We inquire further into the question of the volumes of the hydrocarbon di- derivatives of benzene.

	The methyl ethyl benzenes.		
			
	para	meta	ortho
b.p.	162°	159°	159°
$V_m$	162.3	160.7	160.6
	$\Delta - 1.7$		

Propyl benzene  $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_3$  b.p. 158.6  $V_m$  162.2.

The difference in volume between the ortho and para methyl ethyl benzenes is

$$\Delta = 160.6 - 162.3 = -1.7.$$

From the fact that the volume of the para variety and the volume of propyl benzene are almost identical, we suppose that the methyl and the ethyl groups are independent, but from the fact that there is a diminution of  $-1.7$  in the case of the ortho variety, we conclude that the groups interfere with each other. They are on the same side of the ring and the compound is thus of the adjacent type:—

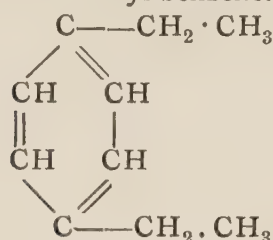
The methyl propyl benzenes.			
para	meta	ortho	
b.p. 175.0	177	182.0	
$V_m$ 184.8	[184.1]	—	
Butyl benzene	$C_6H_5CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$	b.p. 180	$V_m$ 184.8
Iso butyl benzene	$C_6H_5 \cdot CH_2 \cdot CH \begin{smallmatrix} \nearrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$	b.p. 167.5	$V_m$ 177.7
Secondary butyl benzene	$C_6H_5 \cdot CH \begin{smallmatrix} \nearrow CH_3 \\ \searrow CH_3 \end{smallmatrix} \cdot CH_2 \cdot CH_3$	b.p. 171.0	$V_m$ 181.4

These last two compounds illustrate the rule that when unsaturated groups are attached to the benzene nucleus, large contractions in volume are apparent.

The methyl isopropyl benzenes.			
para	meta	ortho	
b.p. 171	176	—	
$V_m$ 184.8	183.6	—	
$\Delta$ b.p. between para and meta 176 - 171 = +5°			
$\Delta V_m$ between para and meta 183.6 - 184.8 = -1.2			

It is remarkable that whilst there is no distinction between the para methyl *n* propyl and methyl isopropyl benzenes as regards volume, the meta normal compound shows a small compression and the meta iso compound shows a larger compression.

Diethyl benzene.

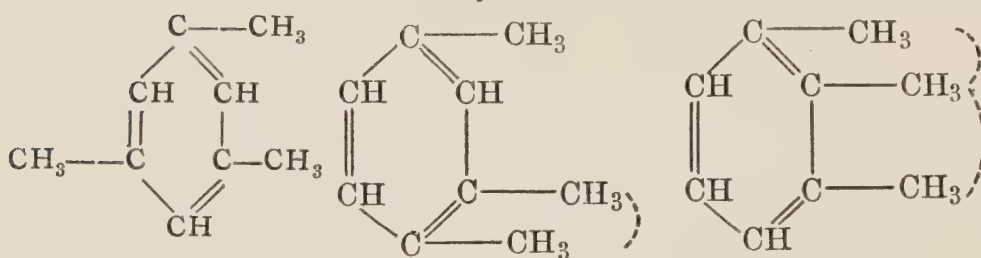
b.p.  $179^\circ$   $V_m$  [185.4]  $d_{15}$  0.8707  $C$  0.520. $\text{C}_6\text{H}_4$  89.6 $2\text{C}_2\text{H}_5$  96.0 $\Sigma nV_a$  185.6 $V_m$  185.4

Tri substituted benzenes.

The trichlor benzenes.

	1 : 3 : 5	1 : 2 : 4	1 : 2 : 3
b.p.	208	213	218
	+ 5		$2 \times + 5$

The trimethyl benzenes.



Mesitylene.

Pseudocumene.

Hemimellitene.

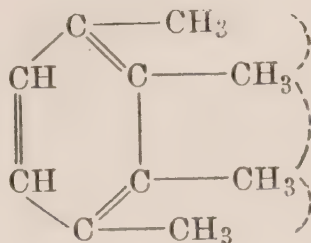
	1 : 3 : 5	1 : 3 : 4	1 : 2 : 3
b.p.	164.5	170	175
	+ 5.5		+ 5
$V_m$	162.8	[160.9]	
	- 1.9		

We see that there is an increase in temperature of  $+ 5^\circ$  for each step of the change from mesitylene to hemimellitene, and a contraction of  $- 1.9$  from mesitylene to pseudo cumene. We cannot doubt that the volume of hemimellitene would be  $162.8 - 2 \times 1.9 = 159.0$  at least.

The tetramethyl benzenes.







Durene.  
b p.  $190^{\circ}$   
 $V_m$  —

Isodurene.  
 $196^{\circ}$   
[ $181.8$ ]

Prehnitol.  
 $204^{\circ}$   
—

Butyl benzene.  
 $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$

b.p.  $180^{\circ}$

$V_m$   $184.4$

$\Delta$ b.p. between butyl benzene and durene	$190^{\circ} - 180^{\circ} = 10^{\circ} = 2 \times 5^{\circ}$
$\Delta$ b.p. between butyl benzene and isodurene	$196^{\circ} - 180^{\circ} = 16^{\circ} = 2 \times 8^{\circ}$
$\Delta$ b.p. between butyl benzene and prehnitol	$204^{\circ} - 180^{\circ} = 24^{\circ} = 3 \times 8^{\circ}$

We thus see that two independent ortho groups occasion a rise in the boiling-point of twice that for a single ortho group. Two *contiguous* ortho groups occasion a rise of twice  $8^{\circ}$  and three contiguous ortho groups a rise of thrice  $8^{\circ}$ .

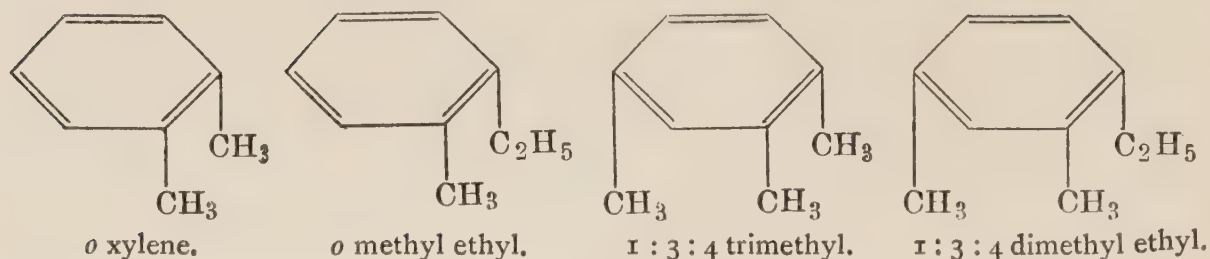
The two contiguous ortho groups of isodurene cause a contraction  $\Delta = 184.4 - 181.8 = -2.6 = 2 \times -1.3$ .

In reviewing the work done in the last section we note that whenever two methyl groups are in association there are augmentations of  $+5^{\circ}$  in the boiling-point and contractions of  $-1.7$ .

Examples.	$\Delta$ .	$\Delta$ .	
<i>p</i> xylene	$140.3$	$-2.4$	one ortho
<i>o</i> xylene	$137.9$		
<i>p</i> methyl ethyl	$162.3$	$-1.7$	one ortho
<i>o</i> methyl ethyl	$160.6$		
1:3:5 trimethyl	$162.8$	$-1.9$	one ortho
1:3:4 trimethyl	$160.9$		
1:3:5 dimethyl ethyl	$184.8$	$-1.6$	one ortho
1:3:4 dimethyl ethyl	$183.2$		
Tetramethyl calculated	$185.2$	$-1.7 \times 2$	two ortho groups (contiguous)
1:2:3:5 tetramethyl	$181.8$		

It is thus concluded that whenever we have two methyl groups in conjunction there are contractions of  $-1.7$  or thereabouts, and as often as this is repeated in a single molecule, we find this contraction.

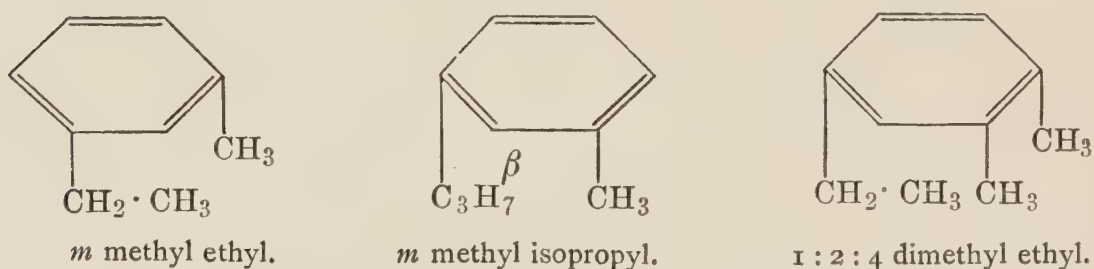
From this it follows that those compounds which have been examined are the "adjacent" varieties and the formulæ of these would be



If the substituents be methyl groups, they are unable to interact when in the meta position relatively to each other, but there are indications that when the chain is lengthened they may do so.

	$V_m$ .	$\Delta$ .	
<i>p</i> methyl ethyl benzene	162.3	- 1.6	one meta
<i>m</i> methyl ethyl benzene	160.7		
<i>p</i> methyl isopropyl	184.8	- 1.2	one meta
<i>m</i> methyl isopropyl	183.6		
1 : 2 : 5 dimethyl ethyl	184.8	- 1.6 × 2	one ortho and one meta
1 : 2 : 4 dimethyl ethyl	181.6		

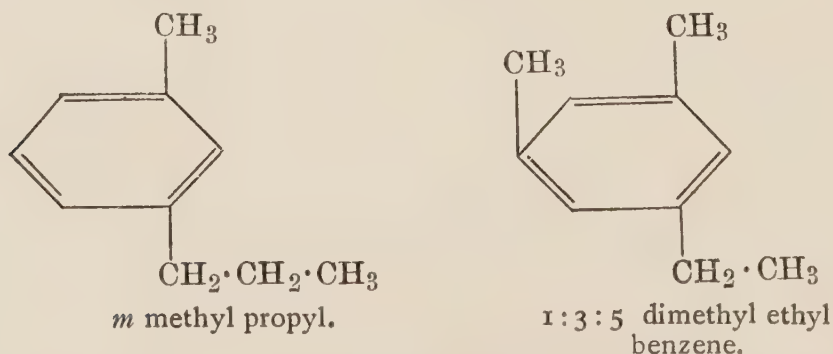
The formulæ are thus



There are exceptions to this, but the volumes are in all cases normal.

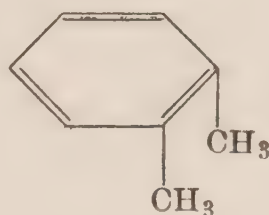
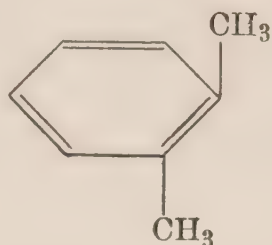
	$V_m$ .	$\Delta$ .
<i>p</i> methyl propyl	184.8	- 0.7
<i>m</i> methyl propyl	184.1	
1 : 3 : 5 dimethyl ethyl	184.8 (1)	- 0.9
1 : 3 : 5 dimethyl ethyl	183.9 (2)	

This, so far as we can see, can only be explained by placing one group in opposition to the others.



We assume that the opposed varieties of the different compounds would have normal volumes because the interaction of groups is impossible.

All this seems to agree with our explanation of the two values for *o* xylene.

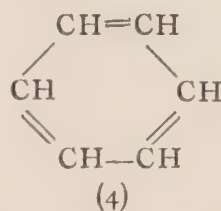
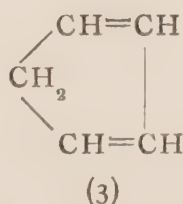
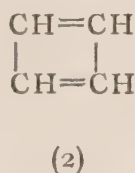
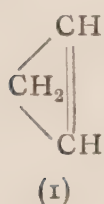


$V_m$	140.2 (Schiff)	{ 137.9 (Pinette) 138.2 (Neubeck)	$\Delta$
$\Sigma n V_a$	140.6		- 2.3 - 2.0

## Complex Aromatic Rings.

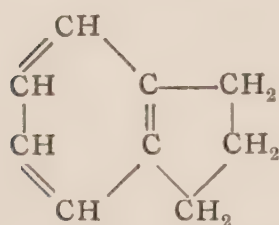
### (a) Condensed.

The benzene nucleus is the only one of the type, which contains a single ring, for which data are available. The following is a series of such hydrocarbons. See Le Bas (*loc. cit.*) and *ref.* :—



Derivatives of all the above hydrocarbons are known except (1), but, as before stated, only (4) has been prepared.

We now proceed to study a series of more complex hydrocarbons, which are wholly or in part of the type just mentioned. The series is made more complete by the use of the formula described in the appendix (q.v.).

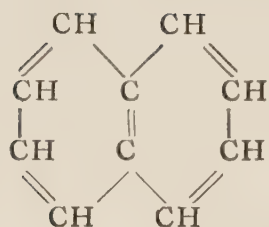


Hydrindene. $C_9H_{10}$			
$d_{15}$	0.957	b.p. 176°	$C = 0.46$
$V_m$	144.0	(by formula)	
$\Sigma n V_a$	170.2	(46 × 3.7)	
$\Delta$ for ring structure =		<u>- 26.2</u>	

One six-membered ring	- 15.0
One five-membered ring	- 12.0 ( <i>vide ante</i> )

$$\text{Total contraction} = \underline{\underline{- 27.0}}$$

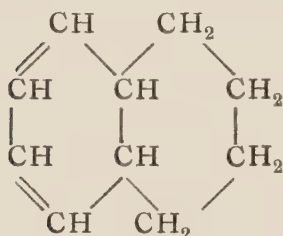


Naphthalene  $C_{10}H_8$ .

$$\begin{array}{r} V_m \quad 147.2 \\ \Sigma_n V_a \quad 177.6 \quad (48 \times 3.7) \end{array}$$

$$\Delta \text{ for ring structure} = - \underline{\underline{30.4}}$$

Since the contraction for a single six-membered ring is  $-15.0$ , the contraction for two such rings is  $-30.0$ . A contraction of this magnitude is seen to apply to naphthalene, a compound containing a condensed ring system, which is evidently equivalent to two separate six-membered rings.

Naphthyl hydride  $C_{10}H_{14}$ .

$$\begin{array}{r} V_m \quad 171.2 \\ \Sigma_n V_a \quad 200.0 \quad (54 \times 3.7) \end{array}$$

$$\Delta \text{ for ring} = - \underline{\underline{28.8}}$$

If we compare naphthyl hydride with naphthalene, we get the following results :—

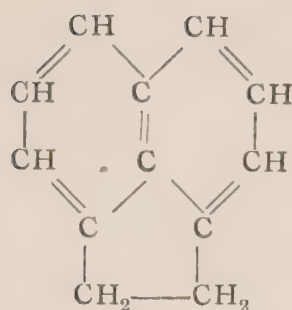
$$\begin{array}{r} [C_{10}H_{14}] = 171.2 \\ [C_{10}H_8] = 147.2 \\ \hline \Delta \text{ for } 6[H] = \underline{\underline{24.0}} \end{array}$$

Again, comparing toluene and hexahydrotoluene, we find—

$$\begin{array}{r} [C_7H_{14}] = 141.8 \\ [C_7H_8] = 118.3 \\ \hline \Delta \text{ for } 6[H] = \underline{\underline{23.5}} \end{array}$$

It is thus seen, that, on reducing a substituted ring of the benzene extra hydrogen atoms possess volumes which are nearer  $4.0$  than to  $3.7$ .

The result is, that the apparent contraction for such a reduced ring, is less than the normal, i.e., by an amount equal to  $6(4.0 - 3.7) = 1.8$ . Thus the contraction for the nucleus really is  $-28.8 - 1.8 = -30.6$ . For naphthalene  $-30.4$ .

Acenaphthene  $C_{12}H_{10}$ .

m.p.  $103^{\circ}$ , b.p.  $277^{\circ}$  d m.p.  $1^{\circ}03$ .  
By formula d.b.p.  $0^{\circ}903$  if  $c = 0^{\circ}46$ .

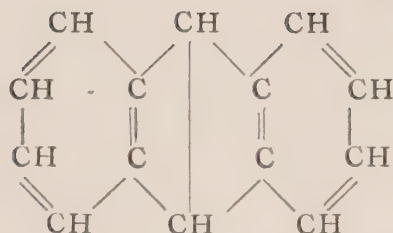
$$V_m = 170^{\circ}5$$

$$\Sigma_n V_a = 214^{\circ}6$$

$$\Delta \text{ for ring} = - \underline{\underline{44^{\circ}1}}$$

Two six-membered rings  $2 \times 15 = 30^{\circ}0$   
One five-membered rings  $= 12^{\circ}0$

$$\text{Total contraction} = - \underline{\underline{42^{\circ}0}}$$

Anthracene  $C_{14}H_{10}$ .

$$V_m 195^{\circ}5$$

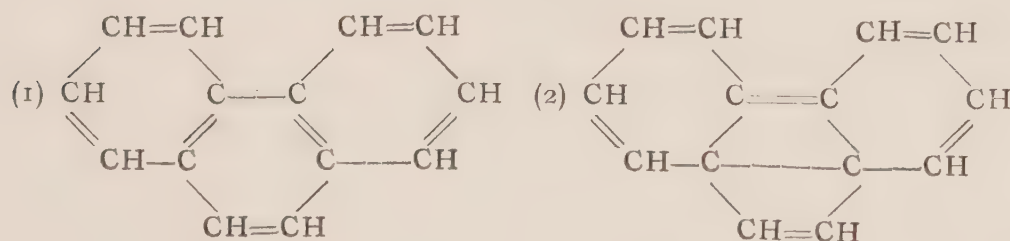
$$\Sigma_n V_a 244^{\circ}2$$

$$A \text{ for ring} = - \underline{\underline{48^{\circ}7}}$$

Two six-membered rings  $= 30^{\circ}0$   
Two four-membered rings  $= 17^{\circ}0 (2 \times 8^{\circ}5)$

$$\text{Total contraction} = - \underline{\underline{47^{\circ}0}}$$

Three six-membered rings would show a contraction of  $3 \times -15^{\circ}0 = -45^{\circ}0$ , from which it follows that the above formula is the correct one.

Phenanthrene  $C_{14}H_{10}$ 

$$V_m 196^{\circ}0$$

$$\Sigma_n V_a 244^{\circ}2$$

$$\Delta = - \underline{\underline{48^{\circ}2}}$$

The contraction for phenanthrene is similar to that for anthracene. It is thus probable that they have similar structure. If this were the case, phenanthrene would have a formula similar to (2) and not like that of (1).

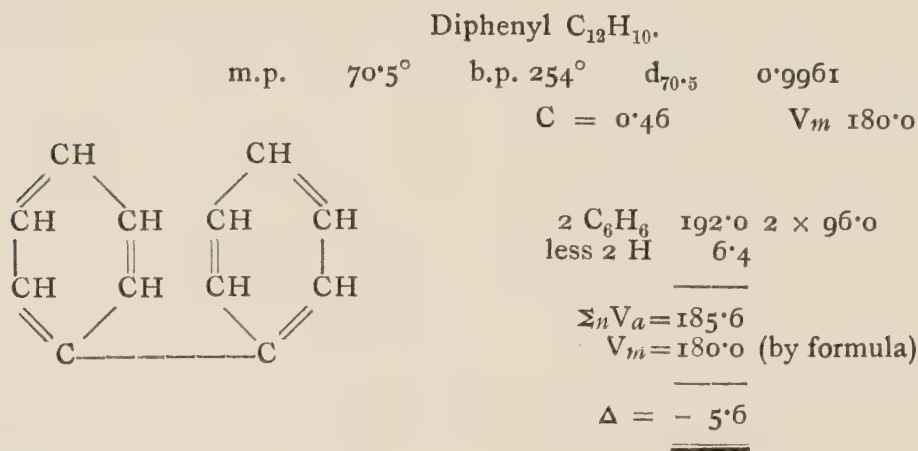
This structure would occasion a contraction of  $-48.0$ .

$$\begin{array}{rcl}
 \text{Two single six-membered rings} & 2 \times 15 & = -30.0 \\
 \text{Two four-membered rings} & 2 \times 8.5 & = -17.0 \\
 \hline
 \Delta & = & -47.0 \\
 \hline
 \end{array}$$

The first formula would show a contraction equal to 3 six-membered rings  $3 \times -15.0 = -45.0$

### (b) Separated Rings.

No data are available for compounds of this type, but with the help of the formula, we may find out how these rings affect the volume.



There is reason to suppose that there is a special constitutive effect associated with the presence of two conjugated unsaturated rings. Accurate data, however, are alone capable of showing this definitely.

### The Polymethylenes $C_nH_{2n}$ .

The aromatic compounds, when reduced, give a series of saturated compounds called the polymethylenes. They are isomeric with the open-chain olefins, and are distinguished from them by the possession of ring structure. Only two or three compounds of this character have been directly investigated, viz. diamylene  $C_{10}H_{20}$ , hexamethylene  $C_6H_{12}$  and its homologues hexahydrotoluene  $C_6H_{11}$  ( $CH_3$ ), hexahydroxylene  $C_6H_{10}$  ( $CH_3$ )<sub>2</sub>.

The values obtained for the others must consequently be calculated values.  $C = 0.46$ , which is a number usually employed when unsubstituted ring compounds are dealt with.



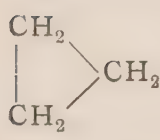
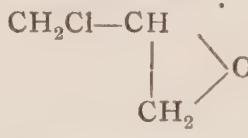
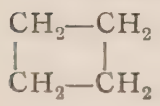
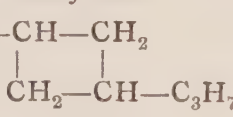
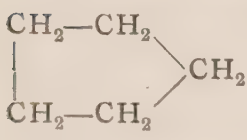
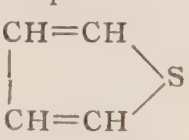
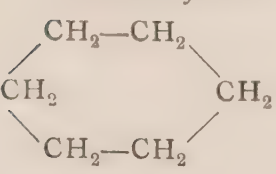
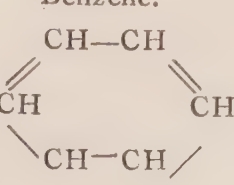
TABLE XXI.—THE POLYMETHYLENES.

Olefins.	$V_m$ .	$\Delta$ for Ring.	$V_m$ .	Polymethylenes.
Propylene $C_3H_6$	66.6	-6.4	60.2	Trimethylene $(CH_2)_3$
Butylene $C_4H_8$	88.8	-8.8	80.0	Tetramethylene $(CH_2)_4$
Pentylene $C_5H_{10}$	110.0	-12.0	98.0	Pentamethylene $(CH_2)_5$
Hexylene $C_6H_{12}$	132.5	-16.0	116.5	Hexamethylene $(CH_2)_6$
Heptylene $C_7H_{14}$	154.8	-20.8	134.0	Heptamethylene $(CH_2)_7$
Octylene $C_8H_{16}$	177.6	-26.4	151.2	Octomethylene $(CH_2)_8$

The diagram on next page shows how the contraction for ring structure varies with the size of the ring.

Confirmative evidence in favour of the above contractions for single-ring structure is found in the following table. Since it is derived from the consideration of derivatives of the simple hydrocarbons, details concerning the derivation of  $\Sigma nV_a$  must be looked for elsewhere.

TABLE XXII.—THE MAGNITUDES OF THE CONTRACTIONS DUE TO RING STRUCTURE.

Polymethylenes.	$V_m$ .	For ring structure.	For ring structure.	$V_m$ .	Other compounds.
Trimethylene— 	60.2	-6.4	-5.2	$\left\{ \begin{array}{l} 87.5 \\ 92.2 \end{array} \right. \Sigma nV_a$	Epichlorohydrin 
Tetramethylene— 	80.0	-8.8	-8.5	$\left\{ \begin{array}{l} V_m. \\ 211.7 \\ 220.2 \end{array} \right. \Sigma nV_a$	Diamylene. 
Pentamethylene— 	98.0	-12.0	-12.4	$\left\{ \begin{array}{l} V_m. \\ 84.9 \\ 97.3 \end{array} \right. \Sigma nV_a$	Thiophene. 
Hexamethylene— 	116.5	-16.0	-15.0	$\left\{ \begin{array}{l} V_m. \\ 96.0 \\ 111.0 \end{array} \right. \Sigma nV_a$	Benzene. 

It cannot be doubted, on the one hand, that the above-mentioned contractions are the true ones, if we allow for the possi-

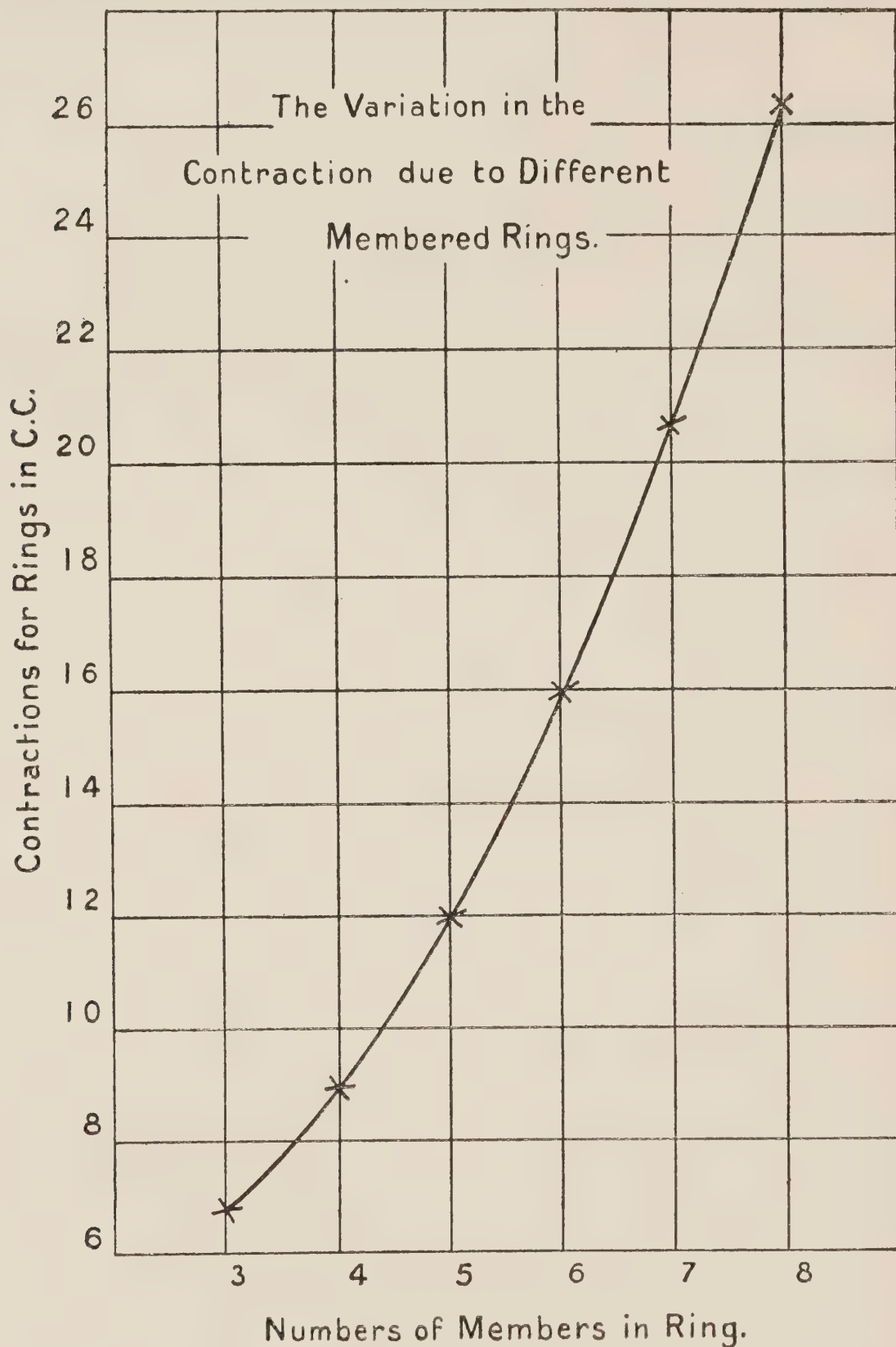


FIG. 2.

bility of a slight variation one way or the other, and on the other hand, that the volumes calculated for the polymethylenes are approximately correct.

The most interesting fact connected with these results is the one already noticed at the commencement of this chapter, viz. that *the contraction for ring structure varies with the size of the ring*. This is the result which we should expect, if the contraction is additive in nature, that is, made up from the sum of small deviations of the individual atomic volumes from the normal. It is, however, remarkable, that those attempts which have been made, to elucidate this question, by means of other physical properties which show a marked effect for ring structure, give results which are opposed to the conclusions arrived at here. The view taken by Sir Wm. Perkin, in his study of molecular magnetic rotations,<sup>27</sup> is, that *the magnitude of the constitutive effect is constant*, and thus not related to the size of the ring. Independently of the question of the probable correctness of this latter view, a study of the question has led us to conclude that it is probably based on a wrong reading of the data. It is remarkable that Perkin at first calculated results which favoured the view, that the magnitude of the effect due to ring-formation varies with the size of the ring; but because these results appeared to him to be anomalous, he discarded this method of calculation for another one which seemed more satisfactory.

TABLE XXIII.—COMPARISON OF TWO METHODS OF CALCULATING THE EFFECTS OF RING FORMATION ON THE MOLECULAR MAGNETIC ROTATIONS OF ORGANIC COMPOUNDS.

No. of Members in Ring.	Substance.	M	For Ring Structure.	For Ring Structure.	M.	Substance.
3	{ Butyric Acid .	4.472	-0.331	-0.599	4.740	Formic Acid + 3CH <sub>2</sub> .
	{ Trimethylene .					Trimethylene.
	{ Carboxylic Acid }	4.141			4.141	{ Carboxylic Acid.
4	{ Valerianic Acid .	5.513	-0.465	-0.546	5.594	Acetic Acid + 3 CH <sub>2</sub> .
	{ Tetramethylene }					Tetramethylene.
	{ Carboxylic Acid }	5.048			5.048	{ Carboxylic Acid.
5	{ Hexylic Acid .	6.530	-0.639	-0.640	6.531	Propionic Acid + 3CH <sub>2</sub> .
	{ Pentamethylene }					Pentamethylene.
	{ Carboxylic Acid }	5.891			5.891	{ Carboxylic Acid.
6	{ n Hexane .	6.646	-0.982	-0.607	8.582	Valerianic + 3CH <sub>2</sub> .
	{ Cyclohexane . }	5.664			7.975	{ Methyl Hexamethylene.
						{ Carboxylic Acid.



The magnitude of the effects for ring formation on the left-hand side of the above table, favour the conclusion arrived at from a study of molecular volumes, whilst those on the left-hand side, which were adopted by Perkin, give a different result.

It is not difficult to show, by making a summation of the atomic values, or by means of a calculation of the series-differences  $S$ , that formic and acetic acids are anomalous, and not only these, but acetone and other compounds employed by Perkin in calculating his results. The average value of  $S$  the Series constant for the acids is 0.393, i.e. for  $O_2$ .

TABLE XXIV.—ACIDS.

Substance.	M.	$\Delta$ .	S.	$\Sigma_{nm}$ .	Difference.
Formic Acid .	1.671		(0.648)	1.410	- 0.261
Acetic „ .	2.525	0.854	(0.479)	2.419	- 0.106
Propionic „ .	3.462	0.937	0.393	3.462	$\pm 0$
Butyric „ .	4.472	1.010	0.380	4.485	+ 0.013
Pelargonic „ .	9.590	5 $\times$ 1.023	0.383	9.600	+ 0.010
The Ketones.					
Acetone .	3.514		(0.445)	3.444	- 0.091
Methyl Propyl } Ketone }	5.499	2 $\times$ 0.992	0.384	5.508	+ 0.009

These first and second members of the respective series are not strictly analogous to the succeeding members as regards their molecular magnetic rotations, any more than they are for other physical properties, and thus they cannot be used to calculate the effects due to ring-formation. The values of  $M$  are relatively high for formic, acetic acid, etc., so that the calculated effects, due to ring structure, are thereby increased. This result makes it appear that the effect is independent of the size of the ring, a conclusion which is seen to be incorrect.

Perkin argued that because trimethylene carboxylic acid is the first member of the series, it should possess an augmented value similar to formic acid. This is not necessarily the case, because the former compound is differently constituted, since it contains a ring, and in any case, the amount of the augmentation differs considerably, even for different open chain compounds. Trimethylene carboxylic acid is sufficiently complex to exclude

the idea of such an augmentation, and it is of nearly the same complexity as butyric acid, with which it may suitably be compared. We believe that the position of a compound in a series has no significance, apart from complexity.

It must also be observed that *magnetic rotary power* is a physical property which is much more sensitive to constitutive influences than molecular volumes, so that even slight changes in structure might considerably affect the values. An apparent difference in the observed and calculated results, and which is relied upon to indicate the extent of some constitutive influence, may consequently be the algebraical sum of several effects. This would vitiate to some extent the calculated effects due to ring structure determined by this property, and probably does so.

In *molecular volumes*, on the other hand, we choose data which are only affected by the constitutive influence in question—ring structure, the others being negligible by comparison.

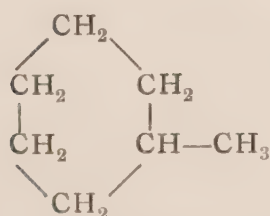
Moreover, the corrections for this structure are very considerable.

*No physical property is probably so well adapted to the elucidation of the ring structure of chemical compounds as that of molecular volumes.*

### The Naphtenes.

These subjects are specially interesting, chiefly owing to the fact that they occur in many mineral oils and other natural products. They do not, however, differ in character from the compounds of the preceding group. The data have been taken chiefly from *Richter's Organ. Chem.* (Smith). Eng. edit. vol. ii., p. 292.

Hexahydrotoluene  $C_7H_{14}$  (Heptanaphtene).



$V_m = 141.8$  (Lossen and Zander).

$$[C_6H_5] = 92.8$$

$$6[H] = 24.0$$

$$[CH_3] = 25.5$$

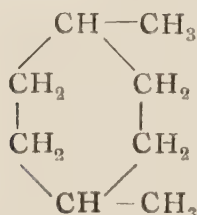
$$\Sigma_n V_a = \underline{\underline{142.3}}$$

For ring formation.	Hexahydrotoluene $C_7H_{14}$	141.8
	Heptylene	154.8

$$\Delta \text{ for ring} = \underline{\underline{-13.0}}$$

This value does not represent the real contraction for ring structure, since in these compounds the six extra hydrogens take up larger volumes (*v.a.*) than is usual with ring compounds.

*p* Hexahydroxylene  $C_8H_{16}$ .



$$V_m = 165.0 \text{ (L. and Z.)}$$

$$[C_6H_4] = 89.6$$

$$2[CH_3] = 51.0$$

$$6[H] = 24.0$$

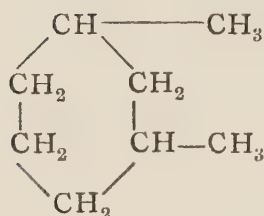
$$\Sigma_n V_a = 164.6$$

For ring formation.	Hexahydroxylene $C_8H_{16}$	165.0
	Octylene	177.6

$$\Delta = \underline{\underline{-12.4}}$$

Hexahydro *m* xylene  $C_8H_{16}$  (octonaphtene).

The value of C for the preceding compound is  $C = 0.506$ .



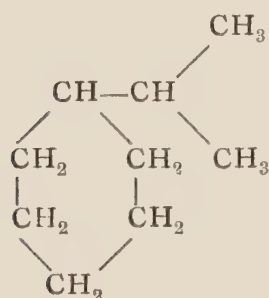
$$\text{b.p. } 118^\circ \quad d_0 \quad 0.7814$$

$$\text{d.b.p. } 0.6782 \quad V_m \quad 165.1 \text{ by formula}$$

$$\Sigma_n V_a \quad 164.6$$

According to theory, there should be little difference between the volumes of this compound and that of the preceding one. This is found to be the case.

Hexahydrocumene  $C_9H_{18}$ .



$$\text{b.p. } 148^\circ \quad d_{20} \quad 0.7870$$

$$C = 0.506 + 0.031 = 0.537$$

$$\text{d b.p. } 0.6766 \quad V_m = 186.2$$

$$[C_6H_5] = 92.8$$

$$[C_3H_7] = 70.0 \text{ (} 19 \times 3.7 \text{)}$$

$$[6H] = 24.0$$

$$\Sigma_n V_a = 186.8$$

$$V_m = \underline{\underline{186.2}}$$

Or from cymene.

$$\text{Cymene } C_6H_4 (CH_3) (C_3H_7) \quad 184.5$$

$$\text{less } CH_3 \quad -25.5$$

$$159.0$$

$$\text{plus H} \quad 3.2$$

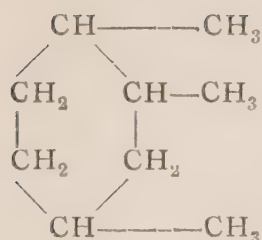
$$162.2$$

$$\text{Six extra hydrogen atoms} \quad 24.0$$

$$\Sigma_n V_a = 186.2$$

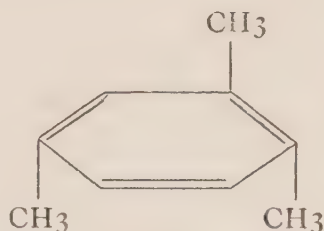
$$V_m = \underline{\underline{186.2}}$$



Hexahydropseudocumene  $C_9H_{18}$  (Nononaphtene).b.p.  $135^\circ$   $d_{12}$  0.7812 (Konowaloff). $C = 0.537$  $d_{b.p.} = 0.6738$  $V_m = 187.0$ Mesitylene  $C_9H_{12}$  162.8  
6H 24.0 $\Sigma_n V_a = 186.8$  $V_m = 187.0$ 

It is necessary to note that although the compound contains two  $CH_3$  groups in the ortho position, an arrangement which is generally accompanied by a contraction of about  $-2.5$ , this does not appear from a consideration of the calculated volumes.

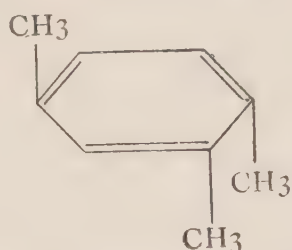
It might be explained by assuming that the particular specimen examined was a compound with the trans or "opposed" configuration.



"Opposed" Hexahydropseudocumene.

We do not, however, wish to lay much stress on this conclusion, since the value is one which has not been found experimentally. The volume of the adjacent form would be

$$186.5 - 2.5 = 184.0.$$



"Adjacent" Hexahydropseudocumene.

### A General Study of the Terpenes.

The data have been taken from *Die Atherische Ole*, Semmler, vol. i., 1906.

(a) *The Hemi-terpenes*  $C_5H_8$ .

Isoprene.

 $V_m = 103.9$  (Buff). $\Sigma_n V_a = 103.6$  ( $28 \times 3.7$ ).

Isoprene is an open-chain diolefin. The volume of valerylene  $C_5H_8$  is 104.2.

(b) *The Olefin Terpenes*  $(C_5H_8)_2$ .

This is a little understood class of compounds. They are probably due to the polymerization of two molecules of one or other of the hemi-terpenes, at least in theory.

The difficulty in calculating the values of these compounds is to know what value for C applies to them.

From di-isoamyl  $C_{10}H_{22}$   $d_{9.8}$  0.7358 b.p. 159.4 (Schiff).  
 $d_{b.p.}$  0.6126.

By calculation we find a value of 0.58 for C. This gives numbers which are about 5.0 units lower than those calculated by the method of summation.

Their theoretical volumes are:—

$$\begin{array}{l} C_{10}H_{22} \text{ (diisoamyl 232} \\ \text{less 6 H - 23} \\ \hline \Sigma_n V_a = \underline{\underline{209}} \text{ or 207.8 by the usual method.} \end{array}$$

TABLE XXV.—THE VOLUMES OF THE OLEFIN TERPENES.  
 (Calculated by Formula.)

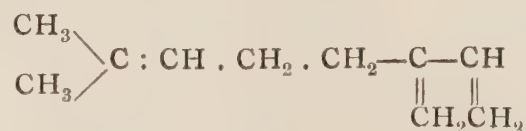
Compound $C_{10}H_{16}$ .	b.p.	$d_t$ .	$V_m$ by Formula	$\Sigma_n V_a$ .	$\Delta$ .
Myrcene . . .	172.0	0.8031 <sub>20</sub> .	203.0	207.8	- 4.8
Alloocimene . . .	188.0	0.8172 <sub>20</sub> .	202.4	„	- 5.4
Anhydrogeraniol . .	172.6	0.8232 <sub>15.5</sub>	198.3	„	- 9.5
Linaloolene $C_{10}H_{18}$	165.8	0.7882 <sub>20</sub>	208.9	214.6	- 5.7

It is difficult to completely account for these numbers by means of the ordinary open-chain formulæ. Since the values are calculated, it follows that we must wait for directly determined data before we can draw certain conclusions.

On the other hand, the nature and origin of the compounds by no means excludes, in some cases at any rate, ring structure.

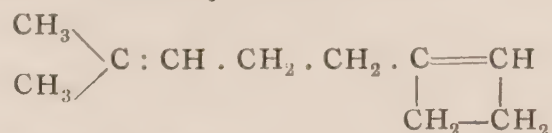
Take, for instance, *myrcene*.

The ordinary formula requires little modification to produce the following:—



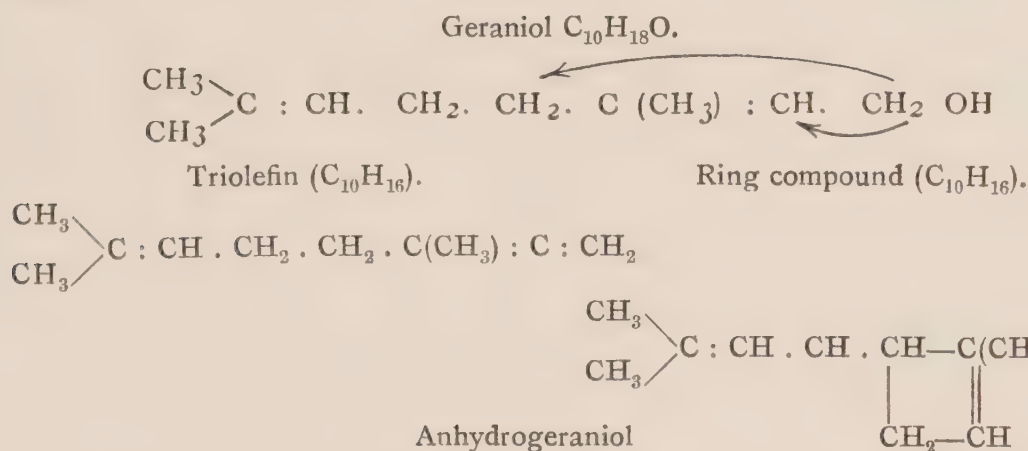
This would cause a contraction of about  $-3\cdot0$ .

From this there is an easy transition to

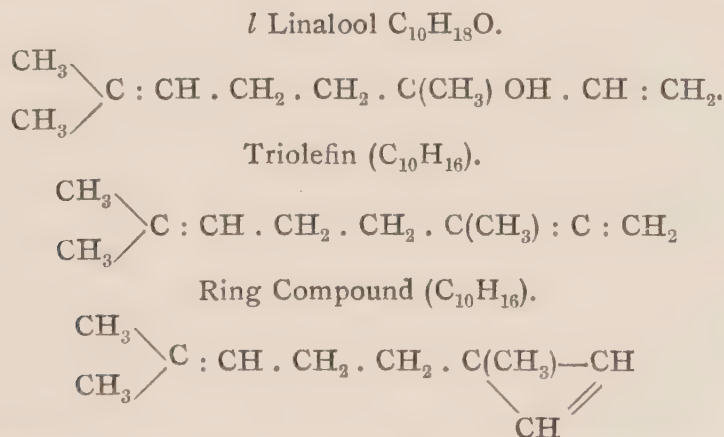


which would cause a contraction of  $-6\cdot0$ .

If we study the formation of the compounds by the dehydration of certain alcohols, we also see the possibility of ring structure.



Both of the above compounds are possible, according as the neighbouring or the fourth hydrocarbon group provides the hydrogen atom which unites with the hydroxyl group to form water.

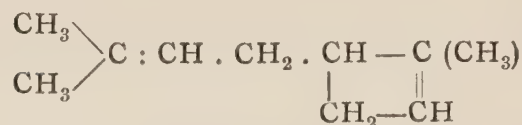


The above triolefin is similar to the preceding one—that is a similar dehydration of geraniol and linalool produces anhydrogeraniol, if the open-chain formula properly describes it.

Linaloolene has two hydrogen atoms more than the compounds of formula  $\text{C}_{10}\text{H}_{16}$ .

We think that it will be found that myrcene, alloocimene and linaloolene are the ordinary open-chain triolefins, but that anhydrogeraniol, or the compound which is called such, is in reality





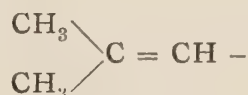
With this conclusion the contraction found in the table is in agreement.

Moreover, the molecular refraction of anhydrogeraniol differs from that of myrcene.

Myrcene.		Anhydrogeraniol.	
$d_{15}$ 0.8025	$\mu_D$ 1.4673	$d_{20}$ 0.8232	$\mu_D$ 1.4835
$M = 46.9$		$M = 47.2$	

The values of  $\Delta$  for myrcene allocimene and linaloolene can, at least in part, be thus explained.

(a) The group



is responsible for a contraction of  $-2.4$  as in  $\beta$  amylene.

(b) The second iso group might cause a contraction of 0.9 as in compounds of complexity  $C_8$ .

Thus

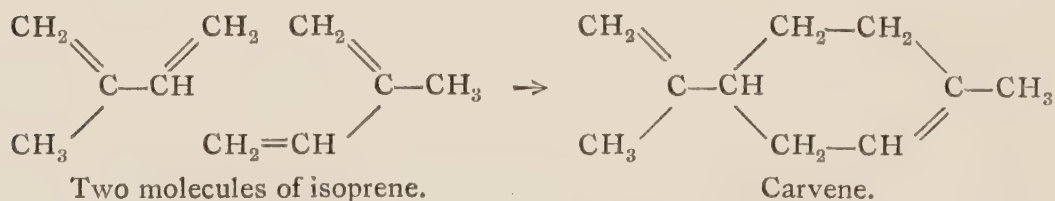
$$\Delta = -2.4 - 0.9 = -3.2$$

$$\Sigma_n V_a = 207.8 - 3.2 = 204.6$$

which is not very different from 203.0, which might be in error by a unit or so.

(c) *The Menthane or Terpan Terpenes* ( $C_{10}H_{16}$ ).

These compounds, which occur in many essential oils, are probably formed by the polymerization of isoprene or some other hemiterpene, with the formation of a ring. Thus:—



The volume of carvene is 190.3 (Schiff).

The observed value for cymene  $V_m$  184.6  
 $\Sigma_n V_a$  184.8

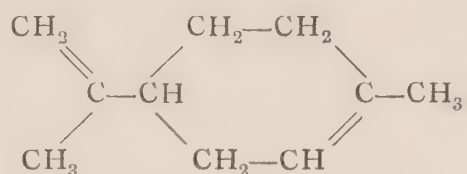
Cymene 184.6  
 less 2 [H]  $-7.4$  for unsaturation  
 of  $C_3H_5$  group.

$C_{10}H_{12}$  177.2  
 Add 4 [H] 12.8 if the four nuclear H atoms  
 are similar to those of benzene.  
 $\Sigma_n V_a = 190.0$  for carvene.

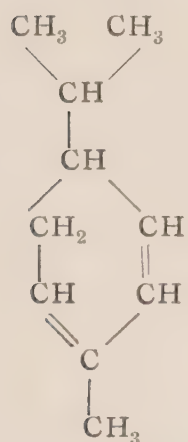
If, on the other hand, the four hydrogen atoms are similar to those in hexahydrotoluene  $[H] = 4.0$ , then the volume would be 193.2, which is about 3 units too large.

The four extra hydrogen atoms are thus equivalent to four hydrogen atoms in benzene.

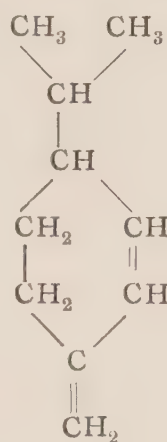
The calculation verifies the formula for carvene.



We may now study the two phellandrenes.



$\alpha$  Phellandrene.



$\beta$  Phellandrene.

$\alpha$ Phellandrene	b.p.	170° C.	$d_{15.5}$	0.846	C = 0.523
$\beta$ „ „ „	„ „ „	„ „ „	„ „ „	0.848	
By formula : $\alpha$ form, 190.2 ; $\beta$ form, 189.7.					

Calculating the volume of the  $\alpha$  form by summation, we find

$$\begin{array}{r}
 [C_{10}H_{14}] = 184.6 \\
 2[H] = \quad 6.4 \\
 \hline
 \Sigma_n V_a = 191.0 \text{ for } \alpha \text{ phellandrene.} \\
 \hline
 \hline
 \end{array}$$

It has been shown that the hydrogen atoms in the nucleus, or those which partially reduce it, may

(a) resemble those of benzene,	$H = 3.2$	$V_m$ 190.3
(b) " " hexahydrotoluene	$H = 4.0$	$V_m$ 193.0.

Carvene has been shown to answer to the first condition, and apparently  $\alpha$  phellandrene also.

Limonene and dipentene on the other hand answer to the second condition.

Limonene	b.p.	177.8	$d_{15.5}$	0.848	$C = .523$	$V_m$ 193.1
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TABLE XXVI.—THE CALCULATED VOLUMES OF THE TERPENES.

Terpenes C <sub>10</sub> H <sub>16</sub> .	b.p.	d <sub>15.5</sub> .	d b.p.	V <sub>m</sub> (calc.).	μ.
{ Limonene . . .	177°-178	0.848	0.7043	193.1	1.4746
{ Dipentene . . .	178	0.848	0.7043	193.1	1.4740
{ Carvene . . .	175	0.853 <sub>20</sub>	0.7159	190.0	by obs. 190.3
{ Sylvestrene . . .	176	0.851 <sub>15.5</sub>	0.7165	189.8	1.4747
{ α Phellandrene . . .	170°	0.846	0.7150	190.2	1.4732
{ β „ . . .	170°	0.848	0.7169	189.7	1.4759
{ Terpinene . . .	180°	0.849	0.7134	190.6	1.4846

Whether these distinctions are valid or not, remains at present uncertain, but in any case the various menthan terpenes possess a range of volume of only 189.7 – 190.6 or at most 189.7 – 193.1.

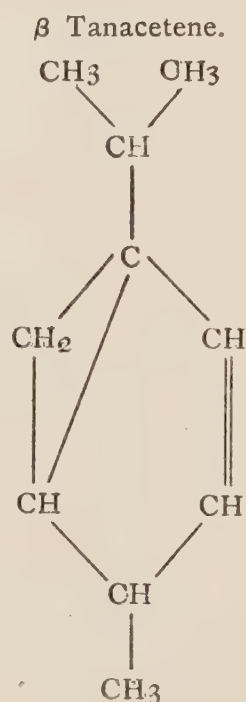
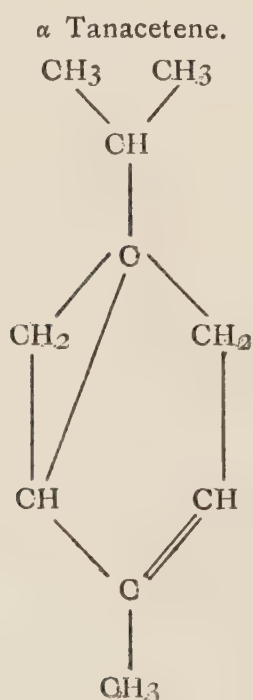
This of course indicates that their structures are so little different, that the molecular volumes are not very much affected by such differences as do occur. These are mostly indicated by the positions of the two ethenoid linkages.

One or two other terpenes of a somewhat different type remain to be noticed.

Thujen      b.p. 151      d<sub>15.5</sub>      0.851.  
If C = 0.523      d b.p.      0.7281      V<sub>m</sub> = 186.5.

The volume of this compound is considerably smaller than the terpenes just enumerated.

The formulæ which have been ascribed to α and β tanacetene are :—





By summation, we find

$$\begin{array}{rcl}
 \text{C}_{10}\text{H}_{14} & 199.8 & (54 \times 3.7) \\
 2\text{H} & 6.4 & \\
 \hline
 \Sigma V_a = & 206.2 & \\
 V_m = & 186.5 & (\text{by formula}) \\
 \hline
 \Delta = & -19.7 & \text{for ring.} \\
 \hline
 \end{array}$$

This contraction is somewhat larger than for a single six-membered ring, viz.  $-15.0$ .

$$\begin{array}{rcl}
 \text{Two four-membered rings} & 2 \times -8.5 = & -17.0 \\
 \text{One three and one five-membered ring} & -6.3 - 12.0 = & -18.3.
 \end{array}$$

The observed contraction is nearer the latter than the former. In any case it is not compatible with the idea of a single six-membered ring, so that tanacetene must be considered to be possessed of a *bi-cyclic* ring.

A further investigation of bi-cyclic compounds of this type is not desirable at present, since the value  $C = 0.523$  which has been applied to ordinary terpenes may not be quite true for these, and we have no means of ascertaining the true value. Direct data for one such compound would furnish the necessary material for such an investigation, but it is at present wanting.

One point of interest exists, which is, that the contraction for a single six-membered ring does not differ much from those marked by what we may call *cross-linking*. This term is used to distinguish these from *bridged rings*. Thus we may mention:—

$$\begin{array}{rcl}
 \square_6 & \Delta = & -16.0 \\
 \square_4 + \square_4 & \Delta = & 2 \times -8.5 = -17.0 \\
 \square_3 + \square_3 & \Delta = & 6.5 + 12.1 = 18.5
 \end{array}$$

The small difference between the contractions for the two classes of compounds makes it difficult to distinguish between them, since a slight difference of this magnitude might be due to small additional constitutive effects.

The following is a list of the *reduction products of cymene*:—

TABLE XXVII.

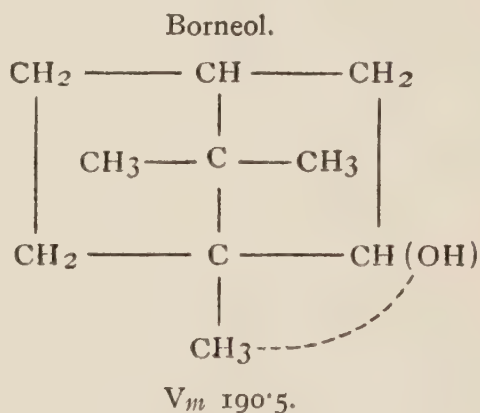
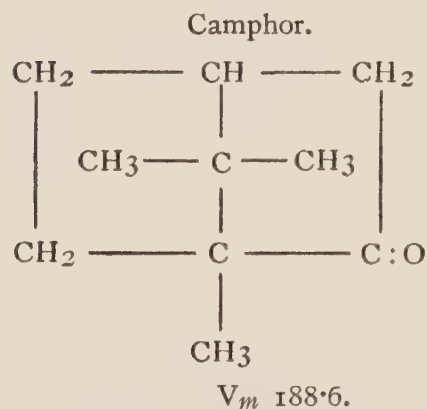
Compound.	$V_m$ .	Apparent effect of ring formation.	$\Sigma_n V_a$ .	C.
Cymene $C_{10}H_{14}$	184.6	- 15.0	184.8	0.523
Carvene $C_{10}H_{16}$	190.3	- 16.9	190.3	"
Menthene $C_{10}H_{18}$	[198.8]	- 15.8	197.4	"
Hexahydrocymene $C_{10}H_{20}$	[208.3]	- 13.0	208.6	"

The six extra hydrogen atoms in the fully-saturated compound hexahydrocymene possess volumes of  $[H] = 4.0$ .

The hydrogen atoms in the nucleus of all the other compounds have been regarded as similar in volume to those of benzene  $[H] = 3.2$ .

(c) *Camphane Terpenes*  $C_{10}H_{16}$ .

These terpenes belong to a second class of ring compounds which are distinguished by the possession of bridged rings. None of these have had their molecular volumes directly determined except pinene, but two derivatives—camphor  $C_{10}H_{16}O$  and borneol  $C_{10}H_{18}O$ —have been determined by Kehrman<sup>28</sup>. These data are sufficient to enable us to ascertain the nature of the rings which are characteristic of this class of compound.



We find by summation—

$$\begin{array}{rcl}
 C_{10}H_{16} & 56 \times 3.7 = & 208.2 \\
 : O & & 11.0 \\
 \hline
 \Sigma_n V_a & & 219.2 \\
 V_m & & 188.6 \\
 \hline
 \Delta = & & \underline{\underline{- 30.6}}
 \end{array}$$

$$\begin{array}{rcl}
 C_{10}H_{18} & 58 \times 3.7 = & 214.6 \\
 . O . & & 7.4 \\
 \hline
 \Sigma_n V_a & & 222.0 \\
 V_m & & 190.5 \\
 \hline
 \Delta = & & \underline{\underline{- 31.5}}
 \end{array}$$

The ring structure of these compounds is thus found to give rise to a contraction of about  $-30$ , which is double that for a single six-membered ring.

In consequence of the absence of data we shall be under the necessity of calculating the molecular volumes by means of the formula. The value of  $C$  is doubtless  $0.460$ , since this value has been found to be appropriate for a large number of ring compounds which do not possess side chains of more than one carbon or equivalent atom.

$$\begin{array}{rcl}
 \text{Camphene } C_{10}H_{16} & \text{m.p. } 48^{\circ} & \text{b.p. } 160^{\circ} \\
 d_{48} \ 0.8481 & C = 0.46 & \\
 d \text{ b.p. } 0.7578 & V_m = 179.5 & \\
 C_{10}H_{16} & 207.2 & \\
 V_m & 179.5 & \\
 \hline
 \Delta & = -27.7 & \text{for ring.}
 \end{array}$$

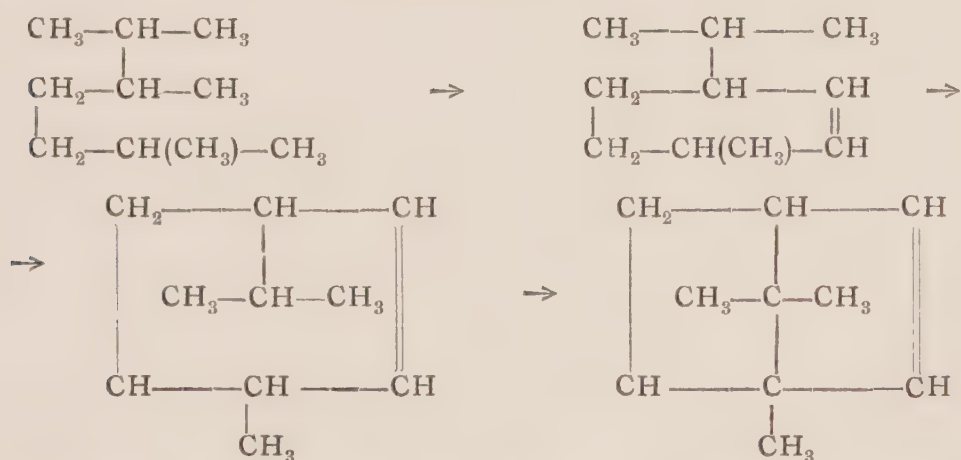
This difference represents the value of the contraction for ring structure, and is much larger than for a single six-membered ring.

We thus conclude that the ring structure is similar to that which has been found for camphor and borneol.

$$\text{For two five-membered rings } \Delta = 2 \times -12 = -24$$

$$\text{For two six-membered rings } \Delta = 2 \times -15 = -30$$

Camphene  $C_{10}H_{16}$  may theoretically be supposed to be formed as follows:—

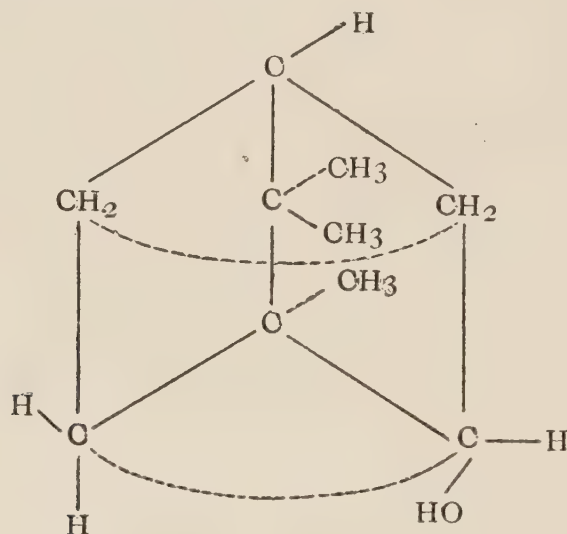


By analogy with camphor and borneol, a compound with the above structure should possess a contraction of about  $-30.0$ . The calculated value is about  $-28.0$ .

As before indicated, two five-membered rings produce a contraction of  $-24.0$ , which is a number considerably below  $-30.0$ .

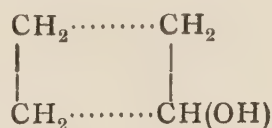


It is difficult to account for this, on the basis of the plane formula, but remembering the tetrahedral arrangement of the carbon valencies, we may substitute the following one, which has also been proposed by O. M. Foster,<sup>28</sup> for bromnitro camphane and other compounds of this type.



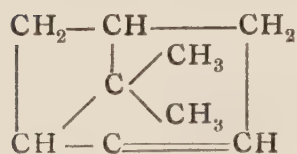
This formula shows the two halves of the camphor molecule forming an angle with each other like a partially opened book set on end.

The carbon groups shown by the dotted line, together with the corresponding ones above, are in a position to influence one another so as to form a potential four-membered ring—



The additional contraction for this, would have to be added to  $-24\cdot0$ , for the two five-membered rings, and so the observed contractions would be partly accounted for.

Pinene  $\text{C}_{10}\text{H}_{16}$ .



b.p.  $156^\circ$     d b.p.  $0\cdot7421$  (Schiff).<sup>29</sup> \*  
 $V_m = 183\cdot2$   
 By formula—     $d_{20} \ 0\cdot858$      $C = 0\cdot46$   
                              d b.p.  $0\cdot7487$   
                               $V_m \ 181\cdot7$   
 Since  $[\text{C}_{10}\text{H}_{16}] = 207\cdot2$

Contraction from observed value  $\Delta = 207\cdot2 - 183\cdot2 = -24\cdot0$

Contraction from calculated value  $\Delta = 207\cdot2 - 181\cdot7 = -25\cdot5$

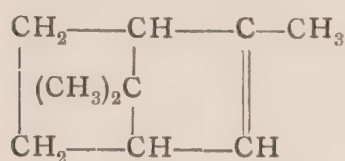
\* The compound with this density was called by Schiff **terpene**, but is probably **pinene**.

The theoretical contraction is on the basis of the plane formula :—

One four-membered ring	— 8.5
One six-membered ring	— 15.0
	<hr/>
	— 23.5
	<hr/>

There is also a difference between the contraction deduced from the data and that indicated by the summation method, as for camphene, but it is not so great.

Fenchene  $C_{10}H_{16}$ .

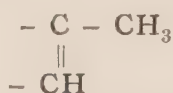


b.p. 160°	$d_{20}$ 0.864
d b.p. 0.752	$V_m$ 180.8
$[C_{10}H_{16}] = 207.2$	
$V_m = 180.8$	
	<hr/>
$\Delta =$	<u>— 26.4</u>

Two five-membered rings  $\Delta = -24.0$

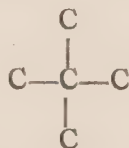
The difference in this case is  $(26.4 - 24) = -2.4$

The result may be due to the grouping

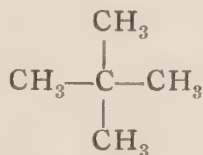


which in  $\beta$  amylene shows a contraction of  $-2.4$ . The idea is that the association of methyl groups and  $||$  gives rise to special contractions.

It is probable that the grouping



which is found centrally, is responsible for a contraction of about  $-1.0$ , as in tetramethyl methane



It is seen that camphor, borneol, and the parent hydrocarbons possess contractions which are very much greater than for single six-membered rings. In fact, bridged rings of some kind are denoted, since, as we have seen, the types of double rings distinguished by cross-linking are not subject to very much larger contractions than for single six-membered rings.

(d) *The Sesquiterpenes* ( $C_5H_8$ )<sub>3</sub>.

We have noticed the following stages in the polymerization of isoprene  $C_5H_8$ .

(i) Two molecules forming the menthan terpenes with a single ring.

(ii) A bridging of the ring.

A further stage is indicated by the union of three molecules of isoprene to form the sesquiterpenes.

Although the compounds  $C_{15}H_{24}$  are all classed as sesquiterpenes, it by no means follows that they are all alike in structure. Indeed it is probable that many types of structure exist.

In any case the value of  $C = 0.46$  may still be employed for the ordinary type of sesquiterpene.

The sesquiterpenes $C_{15}H_{24}$ .				
Clovene	b.p.	262	$d_{15}$	0.932
Cedrene	"	261	"	0.932
Ledene	"	264	"	0.935

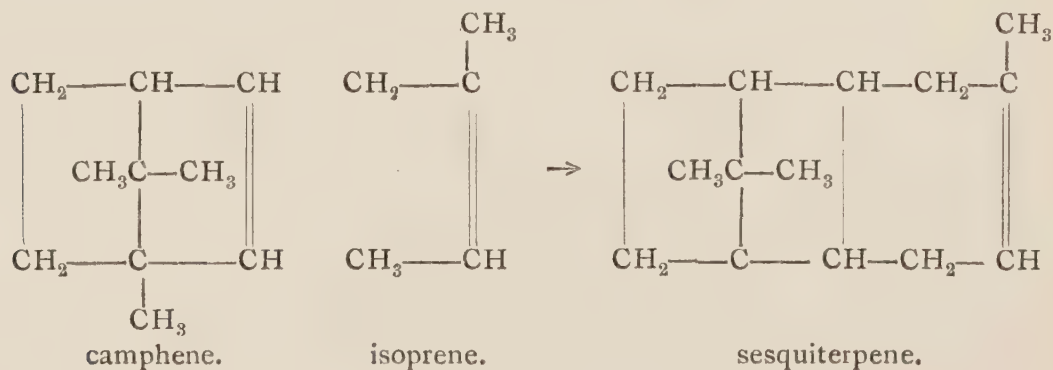
For clovene  $V_m^* = 265.6$ , and a similar value for the others.

By the summation method,

$$\begin{aligned} [C_{15}H_{24}] &= 310.8 (84 \times 3.7) \\ V_m &= 265.6 \\ \Delta &= -45.2 (3 \times -15.0). \end{aligned}$$

Thus the condensation of three molecules of isoprene and the presence of three six-membered rings would account for the molecular volumes obtained.

It is obvious that if the complex molecule consist of three molecules of isoprene, then it must include a bridged ring, that is, a ring which contains a central group linked to two of the peripheral carbon atoms. Otherwise only two six-membered rings would be possible. For our present purpose it is immaterial which of the camphane terpenes forms the basis of the sesquiterpene molecule. We shall assume that it is camphene. Under these circumstances the formula would be





The above molecule should possess a volume of 268.0, which approximately agrees with the number calculated. If the value - 2.4, just shown to be necessary, be deducted, we obtain the calculated value

$$\Sigma_n V_a \ 268.0 - 2.4 = 265.6$$

By formula

$$V_m = 265.6$$

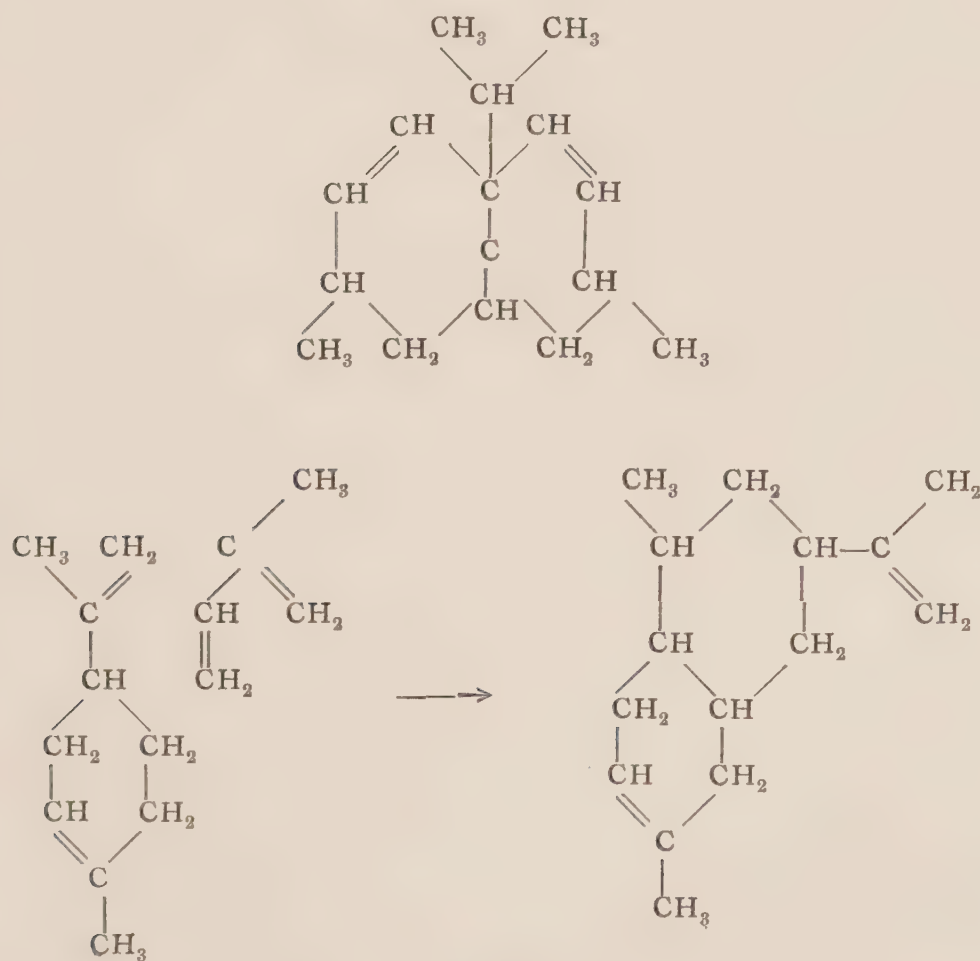
Clovene terminates in an olefin linking, and this is capable of taking on another molecule of isoprene.

Semmler in his *Atherische Öle* classes the following as tri-cyclic:—

Aromadendrene	b.p.	260.5	0.9249 <sub>19</sub>
Clovene		261.2	0.930 <sub>18</sub>
Cedrene		261.2	0.9359 <sub>15</sub>
Ledene		264	0.9349
Vetiden		255	0.9332

and doubtless there are others.

Cadinene is described as



Such a compound as the last would have a volume of

Carvene $C_{10}H_{16}$	190.5
Isoprene $C_5H_8$	103.9
	<hr/>
	294.4
less for six-membered ring	- 15.0
	<hr/>
Volume of cadinene	279.4
	<hr/>

(c) *Diterpenes*  $(C_5H_8)_4$ .

Among the diterpenes we find

Diterpene	b.p.	320°	$d_{15}$	0.9535	$d_{20}$	0.9414
Colophene		318-320°	$d_{15}$	0.940		

Still utilizing the value  $C = 0.46$ .

d b.p.	0.7714	$V_m$	352.4
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we obtain the following results.

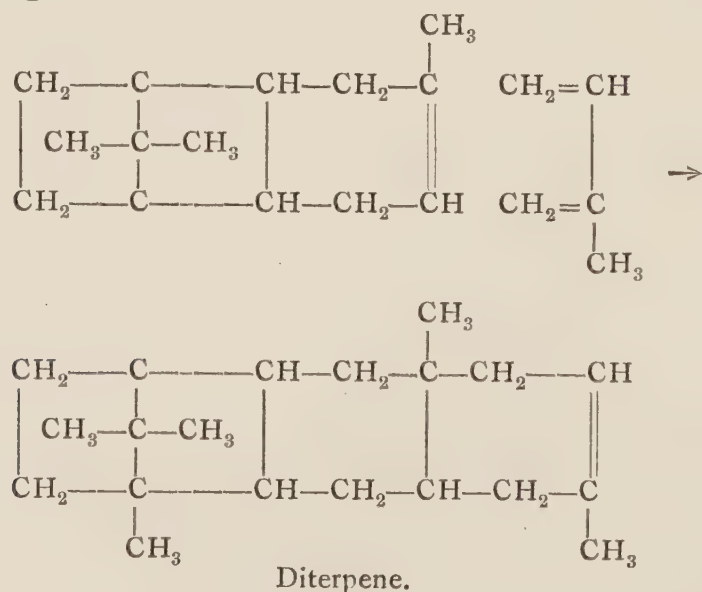
By summation,

$$\begin{aligned}
 [C_{10}H_{20}] &= 414.4 \quad (112 \times 3.7) \\
 V_m &= 352.4 \\
 \Delta &= \underline{\underline{-62.0}} \quad (4 \times -15.5).
 \end{aligned}$$

A better method would be

$$\begin{aligned}
 C_{10}H_{20} &414.4 \\
 \text{less for ring} &\underline{-60.0} \\
 &354.4 \\
 \text{less for } CH_3 \mid \mid &\underline{-2.4} \\
 \Sigma_n V_a &352.0 \\
 V_m &\underline{\underline{352.4}} \quad (\text{by form.}).
 \end{aligned}$$

A formula which would answer to the above description is the following:—

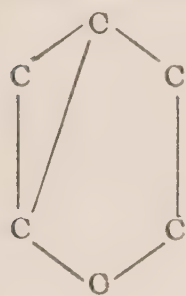


A molecule of this character should possess a volume of about 352.0, and, as it terminates in an olefin link, the polymerization process could continue until compounds of the complexity of india-rubber might result.

### The Effect of Cross Linking. The Double Bond.

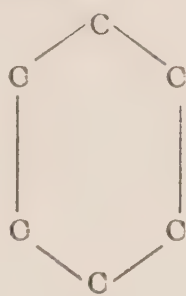
It has been stated that compounds which show the cross-linking, as distinct from those which possess bridged rings, are marked by contractions very little different from those which are characteristic of single rings.

The following are examples of this type of structure with the contractions appropriate to them:—



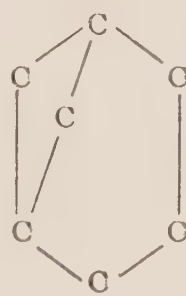
(1)

$$\Delta = \begin{Bmatrix} -6.0 \\ -12.0 \end{Bmatrix} = -18.0$$



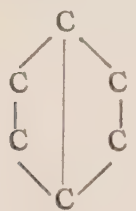
(2)

$$\Delta = -15.0$$



(3)

$$\Delta = \begin{Bmatrix} -8.5 \\ -15.0 \end{Bmatrix} = -23.5$$



(4)

$$\Delta = \begin{Bmatrix} -8.5 \\ -8.5 \end{Bmatrix} = -17.0$$



(5)

$$\Delta = -15.0$$



(6)

$$\Delta = \begin{Bmatrix} -12.0 \\ -12.0 \end{Bmatrix} = -24.0$$

It is also seen that ring (3) does not differ from ring (6) as regards contraction.

The cross linking does not produce any marked effect additional to that produced by a single six-membered ring, *provided that it does not include a C or other atom centrally situated.*

*If it does include such an atom or group,* a very marked influence is exerted on the volume in addition to that produced by the former type of ring, due to an attractive effect of the central carbon atom on the peripheral atoms, and the corresponding reacting effect on the central atoms.



In the *first case*, that of simple cross linking, although it involves the existence of two rings, can scarcely be distinguished from a single ring of the same outline as the first.

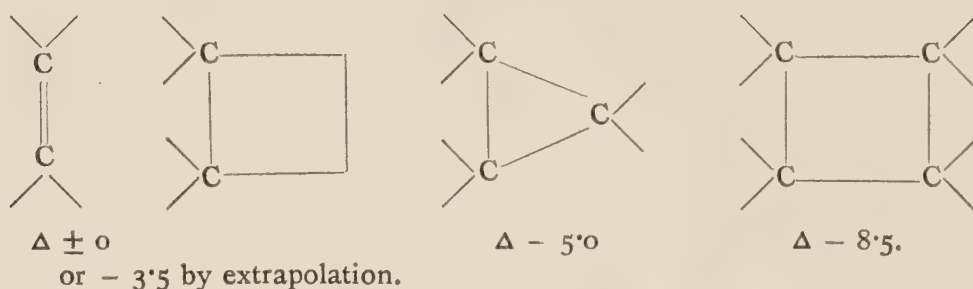
This is unfortunate from the point of view of chemical diagnosis; but if we ascertain beforehand the number of olefin linkings present, by the method of molecular refractions, no difficulty will be experienced in giving the compound its true structure.

The boiling-point is also distinctly lower than for a single ring-terpene,  $150^{\circ}$  or so as against  $170^{\circ} - 176^{\circ}$  C.

### The Olefin Link.

It probably will be a matter for remark that the olefin link does not occasion any apparent contraction at the boiling-point. If we consider the curve showing the contractions for a series of ring compounds—the polymethylenes, for example, we shall find that on extrapolation from *Diagram (2)* p. 48, the olefin link would correspond to a considerable contraction.

There is, however, found to be no contraction. This result calls for an explanation.



If we apply the same principle to the double bond as was brought out by cross-linked rings, we find an explanation of the zero value.

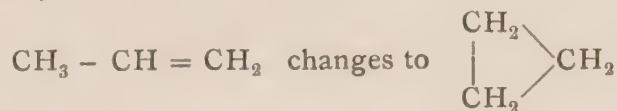
The principle involved is as follows: (a) *In simple cross linking* the changed direction of the link probably does not by itself involve any change in the shape or structure of the molecule, and thus there is no great change in magnitude of the contraction. It is only when an atom or group are included, that a considerable modification takes place in the shape. Under these circumstances the magnitude of the contraction is greatly changed.

(b) In the *olefin type of linking*, or for that matter the acetylene

type, no change in the structure is discernible from that characteristic of the saturated atom for the reason stated.

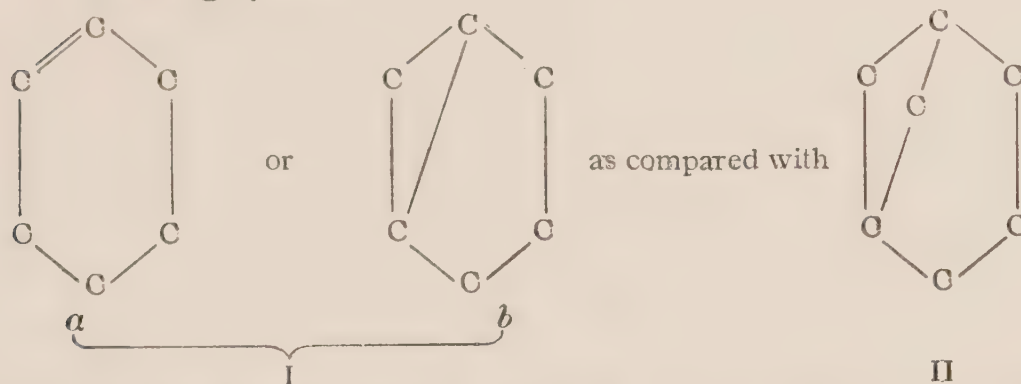


When, however,



a modification in the constitution has occurred, which is at once noticed in the volume.

In the ring system



it is evident that structure I (b) does not occasion any marked change in the shape or volume of the molecule, because the affinity is directed to the penultimate carbon atom, instead of to the neighbouring one. It is simply a case of change in the direction of the affinities. *The shape and volume of the molecule are chiefly determined by the single linkings of the six-membered ring.*

In II, there is included a carbon or alkyl group, and this exercises a modifying influence on the volumes of the peripheral carbon atoms, and so on the molecule.

*In compounds with an olefin link* the atoms are not more favourably situated to act on each other than in the saturated chain. No change in the volume occurs, that is, there is no special action due to unsaturation, at least under the circumstances.

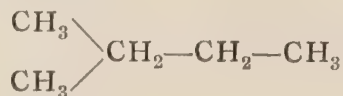
In the *trimethylene ring*, as compared with an open-chain compound with an olefin link, the atoms *are* more favourably situated for interaction, owing to the greater concentration of matter, for the change in the direction of one of the carbon valencies, involves a change in the position of one of the methylene groups, relative to the others.

Thus owing to the distortion of the original straight-chain molecule, there is a *contraction* in volume.

This occurs

when  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$

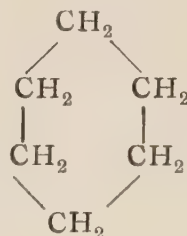
changes to



when

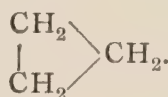
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$

changes to



or when  $\text{CH}_3\text{—CH}=\text{CH}_2$

changes to



In all these cases the affinity forces *are more effective* than in linear arrangement because of *the greater concentration of matter*.

It is also for this reason that the structure which has been named *partial ring structure* involves very noticeable contractions, although not so large as for completed rings. The curvature of the hydrocarbon chain results in diminished volumes, owing to the greater concentration of matter, as compared with what we call straight-chain compounds.

These results are thus just what we should expect, if we assume that the carbon atoms or hydrocarbon elements of the molecule exert an action of affinity on each other, not only in the direction of the linkings but in other directions as well. The greater relative efficiency of the attractive forces makes it impossible for the expanding heat forces to be so effective, and so there are contractions.

It would appear that the above facts can be included in a single generalization which may be stated in the following terms:—

*When any molecular change involves a change in its configuration, that is when one or more atoms are displaced relatively to the others, then there is a distinct effect on the molecular volume. When, however, the change includes simple displacement or a change in the direction of a linkage only, no marked effects on the molecular volume occur.*

*Conversely, modifications of the molecular volumes of compounds, other than those due to simple changes in composition, may be referred to changes in the shape of the molecule.*



This generalization apparently covers all, or nearly all of the constitutive effects which have been noted in connexion with carbon compounds and is doubtless of great importance.

### Ring Systems.<sup>30</sup>

Ring systems are divisible into the following classes:—

- (a) Simple ring systems. Example, Benzene.
- (b) Multiple ring systems.
  - (i) Condensed—naphthalene.
  - (ii) Separated rings—diphenyl.

If  $n$  be the number of carbon atoms in the compound and  $N$  the number of atoms or groups in the ring, we are able to find the nature of the molecule by the amount of the contraction per atom given in the following table:—

TABLE XXVIII.—CONTRACTIONS, ETC., FOR DIFFERENT SIMPLE RINGS.

	No. of atoms in ring. $N$	Contraction.	$\frac{\text{Contraction}}{N}$
Three-membered	3	– 6.0	– 2.0
Four-membered .	4	– 8.5	– 2.12
Five-membered .	5	– 12.0	– 2.40
Six-membered .	6	– 15.0	– 2.50
Seven-membered	7	– 20.8	– 2.97
Eight-membered	8	– 26.0	– 3.25

The last column is especially useful in distinguishing condensed from separated rings.

In these, if the number of C atoms or others like O, S, N be  $n$  and the number of groups, as measured by the contractions be  $N$ , then  $N > =$  or  $<$  than  $n$ .

#### (a) Condensed Rings.

Example, naphthalene  $C_{10}H_8$ .

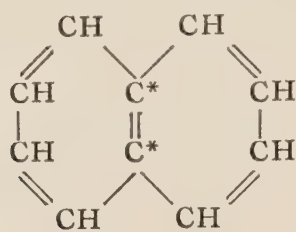
In this case  $N - n =$  a positive number.

The contraction is – 30.0. Dividing this by an average value of  $\frac{C}{N} = 2.50$ , we find that the number of groups by calculation or  $N$

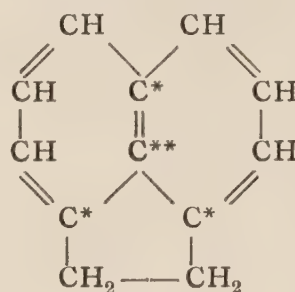
$$- \frac{30.0}{2.5} = 12.$$

$$N - n = 12 - 10 = 2, \text{ that is } N > n \text{ by } 2.$$

Since the number of carbon atoms in  $C_{10}H_8$  or  $n$  is 10.0, then we conclude that naphthalene contains a *double-condensed ring system*, and that there are two atoms common to both rings.



Naphthalene.



Acenaphthene.

In *acenaphthene*  $C_{12}H_{10}$  (condensed ring) the contraction is - 45.0, and a similar calculation can be made.

$$\frac{\Delta}{2.5} = 18 \text{ or } N$$

$$N - n = 18 - 12 = 6$$

There are at least three rings in the compound.

If we observe the diagram, we shall see that three carbon atoms are marked by \* and one by \*\*. This is to indicate that in the one case three carbon atoms are common to two rings, and in the other one carbon atom is common to three rings.

This is somewhat more than a formal statement, because it indicates that the three common C atoms are subject to *double* the compression that the other or peripheral carbon atoms are, and in the other case the single carbon atom has *thrice* the compression.

There is a fundamental principle at the back of these contractions, which is, that the mutual attractive influences exist, which result in diminished volumes. The result is, therefore, that if the contraction is contributed to by the action of one carbon atom on all the others, it, in a similar manner, is acted upon by the other atoms, and so the contraction is doubly affected.

It is, however, to be observed that the C atom of one ring does not influence the carbon atom of another ring unless it forms part of this ring.

The presence of side chains, of course, complicates matters, but in this instance

$$n > N$$

so that the formula for the compound can be fairly well made out.

(b) Separated Rings.

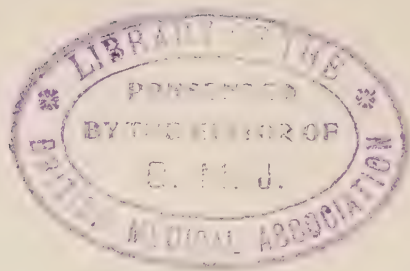
Example, diphenyl  $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5$

In this case  $N - n = 0$

A calculation similar to the above will indicate the nature of the ring system.

The existence of other constitutive effects besides that of ring structure of course makes it more difficult to assign a formula.





## CHAPTER III.

### THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS CONTAINING THE HALOGENS.

#### The Halogens.

KOPP calculated the volumes of chlorine, bromine, and iodine in the combined state as :—

$$[\text{Cl}] = 22.8 \quad [\text{Br}] = 27.8 \quad [\text{I}] = 37.5,$$

which he showed were not very different from their free values.

$$\begin{array}{lll} [\text{Cl}] = 22.7 & [\text{Br}] = 26.8 & [\text{I}] = [34.0] \\ \text{(Kopp)} & \text{(Thorpe).} & \text{(Billet).} \end{array}$$

Those proposed in the present treatise are similar :—

$$[\text{Cl}] = 22.1 \quad [\text{Br}] = 27.0 \quad [\text{I}] = 37.0.$$

The halogens are all monovalent, and in this respect, as perhaps in others, they resemble hydrogen.

#### *Fluorine F.*

Compounds of the type R - F have not been investigated. Only one or two data for fluorine compounds exist altogether. They are :—

$$\begin{array}{rcl} \text{C}_6\text{H}_5\text{F} & 101.6 & \text{(Young)} \\ \text{C}_6\text{H}_5 & 92.8 & \\ \hline \text{F} = & 8.8 & \\ \hline \hline \text{As F}_3 & 53.8 & \text{(Thorpe)} \\ \text{As} & 27.8 & \\ \hline 3 \text{ F} = & 26.0 & \\ \hline \hline \text{F} = & 8.7 & \end{array}$$

In order to confirm, if possible, the above value, a few compounds, indiscriminately chosen from chemical literature, have been studied by means of the formula.

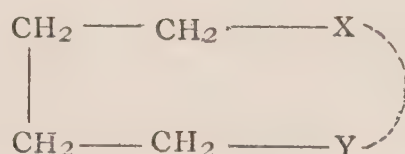
Before calculating the values, it will be necessary to know those values of C which are applicable to such compounds.

TABLE XXIX.

Substance.			$d_{b.p.}$		C.
$\text{CH}_2 : \text{CH} . \text{CH}_2\text{Cl} .$ . . .	$d_0$	0.9610	$d_{46}$	0.9002	0.468
$\text{CH}_3 . \text{COCl} .$ . . . .	„	1.1377	$d_{51}$	1.0570	0.482
$\text{CH}_2\text{Br} . \text{CH}_2\text{Br} .$ . . . .	„	2.2132	$d_{131}$	1.9312	0.450
Mean value of C . . . . .					0.467

It should also be noticed that when atoms like F, Cl, Br and I occupy the  $\alpha$  and  $\beta$  positions in the hydrocarbon chain, there are contractions. These contractions have been shown to be due to a curved configuration of the hydrocarbon chain (*vide prox*).

Thus:—



It will be shown that the above configuration is responsible for a contraction, the magnitude of which is dependent on the size of the partial or potential ring. A few such examples are:—

TABLE XXX.

Substance.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$\text{CH Br} : \text{CH Br} .$ . . .	91.4	93.0	— 1.6
$\text{CH}_2\text{I} . \text{CH}_2\text{Cl} .$ . . .	101.3	103.3	— 2.0
Mean value . . . . .			— 1.8

TABLE XXXI.—THE VOLUME OF FLUORINE (BY CALCULATION).

Substance.	b.p.	$d_t$ .	$V_m$ .	Sum. of at Vols. — 1.8.	F.
$\text{CH F}_2 . \text{CH}_2\text{I} .$ . . .	89.5	2.2412 <sub>12</sub>	94.1	65.9	$2 \times 9.1$
$\text{CH F Br} . \text{CH}_2\text{Br} .$ . .	121.5	2.2633 <sub>10</sub>	103.0	95.9	7.1
Mean for F . . . . .					8.4

Data due to F. Swartz.<sup>31</sup>

If we consider the probable errors incident to this indirect method of calculation, we must conclude that the result is in good agreement with the former values.

The value already obtained for fluorine, viz. :—

$$[F] = 8.7$$

is thus the correct one.

### *Chlorine Cl.*

In considering homologous series such as those of the alkyl halogen compounds, it should be borne in mind that the atomic volumes, calculated by the usual method of differences, are liable to be affected by influences which are of a constitutive nature, and which really act on all the atoms of a molecule. It follows that the results obtained by this means are likely to be different from the true values.

The errors to which this method of calculation is liable, are considerably diminished, if we take the average of a large number of results, but this really amounts to ignoring differences below a certain magnitude.

There is an alternative method which is not based upon comparisons at all, but which enables us to calculate the atomic volumes from a consideration of individual compounds. This method depends upon a principle found to hold in the hydrocarbon series, and which is, that the relative volumes of the atoms are maintained in any series of similarly constituted compounds. Thus the relation  $[C] = 4[H]$  is generally true. The principle in question is that of *constant atomic volume ratios*.

It is possible that the ratios between the atomic volumes may not be quite the same as those assumed, but this error would not appreciably alter the form of the curves obtained. These consequently indicate the nature of the changes in the volumes of the atoms from compound to compound in a series.

### Hydrochloric acid HCl.

$$\text{By D. Bertholet's formula, } V = \frac{M}{D} = \frac{11.1 T_K^2}{P_K(2T_K - T)}$$

$$T_K = 325^\circ \text{ C} \quad P_K = 86 \text{ atmos.} \quad T_{\text{b.p.}} = 238^\circ \text{ C.}$$

$$V_m = 33.1.$$

The volumes of the following compounds are considerably in excess of the normal.



TABLE XXXII.

Substance.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
HCl . . .	33·1	25·8	+ 7·3
CH <sub>3</sub> . Cl . .	50·4	48·0	+ 2·4
C <sub>2</sub> H <sub>5</sub> Cl . . .	71·7	70·1	+ 1·6

Such abnormally large volumes are characteristic of the initial members of most series. In these cases they may be due to the influence of the hydrocarbon and hydrogen elements, since the volumes of methane and ethane are considerably in excess of the volumes which we should expect them to have, from a comparison with succeeding members of the paraffin series.

In any case, it is probable that the volatile hydrogen is responsible for these augmentations. It will be borne in mind that the free and combined values of chlorine are similar.

Free value [Cl] = 22·7. Combined value [Cl] = 22·1.

TABLE XXXIII.—THE ALKYL CHLORIDES.

Substance.	$V_m$ .	Vols. of Hydrocarbon Groups.	Cl.
C <sub>3</sub> H <sub>7</sub> Cl . . .	91·7	70	21·7
C <sub>4</sub> H <sub>9</sub> Cl . . .	113·5	92·3	21·2
C <sub>5</sub> H <sub>11</sub> Cl . . .	135·3	114·1	21·2
Mean value [Cl] = 21·4			

It is probable that chlorine, like carbon, is an integral number of times larger than hydrogen. This is seen from the following—

$$\begin{array}{rcl}
 \begin{array}{l} \text{C}_3\text{H}_7\text{Cl} \quad 91\cdot7 \\ \text{C}_3\text{H}_5\text{Cl} \quad 84\cdot4 \\ \hline 2[\text{H}] = 7\cdot3 \end{array} & \begin{array}{l} \text{C}_4\text{H}_9\text{Cl} \quad 113\cdot5 \\ \text{C}_5\text{H}_{11}\text{Cl} \quad 135\cdot3 \\ \hline [\text{CH}_2] = 21\cdot8 = 3 \times 7\cdot3 \text{ (approx.).} \end{array}
 \end{array}$$

Since [Cl] = 21·4 = 3 × 7·2 (approx.)

It follows that [CH<sub>2</sub>] = [Cl] = 6[H].

This relation enables us to find the number of hydrogen equivalents W in a series, and so the volume V/W of such an

equivalent. These values show how the volume of the atom hydrogen varies in a particular series.

TABLE XXXIV.—THE VOLUMES OF V/W IN THE ALKYL CHLORIDES.

Substance.	W.	V <sub>m</sub> .	V/W.
HCl . . .	7	33·1	4·728
C <sub>2</sub> H <sub>5</sub> Cl . .	19	71·7	3·774
C <sub>3</sub> H <sub>7</sub> Cl . .	25	91·7	3·668
C <sub>4</sub> H <sub>9</sub> Cl . .	31	113·5	3·661
C <sub>5</sub> H <sub>11</sub> Cl . .	37	135·3	3·657

*The Unsymmetrical Polychlorides.*

The successive substitution of chlorine for hydrogen in methane (CH<sub>4</sub>) or ethane (C<sub>2</sub>H<sub>6</sub>) does not correspond to equivalent differences in the volumes or the boiling-points.

TABLE XXXV.

Substance.	b.p.	Δ b.p. for Cl – H	V <sub>m</sub> .	Δ for Cl – H
CH <sub>4</sub> . . . . .	– 164°		38·0	
CH <sub>3</sub> Cl . . . . .	– 24°	140		12·4
CH <sub>2</sub> Cl <sub>2</sub> . . . . .	+ 41·6°	65·6	50·4	14·7
CHCl <sub>3</sub> . . . . .	61·2°	19·6	65·1	19·4
CCl <sub>4</sub> . . . . .	76·7°	15·5	84·5	19·2
CH <sub>3</sub> . CH <sub>3</sub> . . . . .	– 93°		103·7	
CH <sub>3</sub> . CH <sub>2</sub> Cl . . . . .	– 93°	105·5	56·7	15·0
CH <sub>3</sub> . CH <sub>2</sub> Cl . . . . .	+ 12·5°	71·0	71·7	17·2
CH <sub>3</sub> . CHCl <sub>2</sub> . . . . .	83·5°	11·0	88·9	19·1
CH <sub>3</sub> . CCl <sub>3</sub> . . . . .	74·5°		108·0	

We see that in both series there is a decrease in the boiling-point, and an increase in the volume for every substitution of chlorine for hydrogen.

In the following table which shows the values of chlorine in the different compounds, we assume that the volumes of carbon and hydrogen are similar to their values in the hydrocarbons.

TABLE XXXVI.—THE POLYCHLORIDES.

Substance.	$V_m$ .	Volume of Hydrocarbon Group.	$n$ Cl.
R—Cl . . . .			21.5 (average)
CH <sub>2</sub> Cl <sub>2</sub> . . . .	65.1	22.1	2 × 21.5
CHCl <sub>3</sub> . . . .	84.5	18.5	3 × 22.0
CCl <sub>4</sub> . . . .	103.7	14.8	4 × 22.2
CH <sub>3</sub> . CHCl <sub>2</sub> . . . .	88.9	44.5	2 × 22.2
CH <sub>3</sub> . CCl <sub>3</sub> . . . .	108.0	40.8	3 × 22.4

Since  $[\text{Cl}] = [\text{CH}_2]$

$$[\text{Cl}] = \frac{1}{4} \times [\text{CH}_3 \text{ CH Cl}_2] = \frac{1}{4} \times 88.9 = 22.2.$$

This value is similar to the one found in the table by another method.

*We conclude that the average volumes of the chlorine atoms increase as they accumulate in molecules of the above type.*

As an alternative to the above, we may assume that two chlorines possess volumes of  $\text{Cl} = 21.5$  and two of volumes  $\text{Cl} = 23.0$ . The above assumption is, however, the simplest.

#### Bromine Br.

The free value according to Thorpe is—

$$2[\text{Br}] = 2 \times 26.74.$$

In the monobromides we find—

Substance.	$V$ .	$\Sigma_n V_a(\text{R})$ .	$\Delta$ .	
CH <sub>3</sub> Br	55.7	26.0	29.7	+ 2.6

This positive value represents the excess above that which may be considered normal.

TABLE XXXVII.

Substance.	$V_m$ .	R.	Br.
C <sub>3</sub> H <sub>7</sub> Br . .	97.3	70.0	27.3
C <sub>4</sub> H <sub>9</sub> Br . .	118.6	92.3	26.3
C <sub>5</sub> H <sub>11</sub> Br . .	141.2	114.1	27.1

The average volume of bromine is about

$$[\text{Br}] = 27.0.$$



*The Polybromides.*

TABLE XXXVIII.

Substances.	$V_m$ .	Br.
R - Br . .		26.9 (average)
CH <sub>2</sub> Br <sub>2</sub> . .	77.6	27.7
CHBr <sub>3</sub> . .	103.5	28.3
CBr <sub>4</sub> . .	(Not studied)	(probably larger)
Mean value . . .		27.6

The observation that the substitution of a negative atom for a positive one involves an increase in the atomic volume, is repeated in the polybromides, provided these halogen atoms are attached to the same carbon atom.

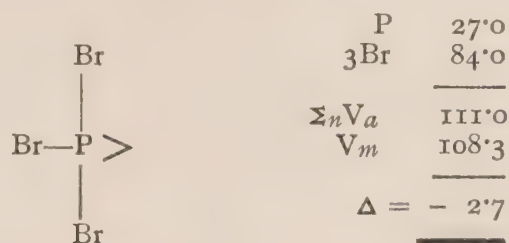
The values for bromine which have been shown, increase progressively as the number of such atoms united to a single carbon atom increases. The volume of bromine may, as already indicated, tend to a higher value, viz. 28.0 or even 28.5.

The following compounds are noteworthy :—

CBrCl <sub>3</sub>	108.4	CCl <sub>3</sub>	80.8	Br 27.5
POBrCl <sub>2</sub>	107.38	POCl <sub>2</sub>	101.37 - 22.0 = 79.37	Br 28.0
	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$		$\begin{array}{c} \text{Br} \\   \\ \text{H}-\text{C}-\text{Br} \\   \\ \text{Br} \end{array}$	
	[Cl] = 22.2		[Br] = 28.3	
	Cl—Hg—Cl		Br—Hg—Br	
	[Cl] = 22.1		[Br] = 28.5	[Hg] = 18.9
	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{Si}-\text{Cl} \\   \\ \text{Cl} \end{array}$		$\begin{array}{c} \text{Br} \\   \\ \text{Br}-\text{Si}-\text{Br} \\   \\ \text{Br} \end{array}$	
	[Cl] = 22.2		[Br] = 28.0	[Si] = 34.0

These numbers show that in an ordinary chloride or bromide, the value for chlorine is 22.1, and that for bromine 28.0.

One remarkable exception is found, viz. P Br<sub>3</sub>.



The volume of bromine is seen to be smaller than in most of the other bromine compounds, in which it is 28·0.

If we suppose that

$$\begin{aligned}
 [\text{Br}] &= [\text{P}] = 27\cdot0, \text{ then} \\
 \Sigma_n V_a &= [\text{P}] + 3[\text{Br}] = 27\cdot0 \times 4 = 108\cdot0
 \end{aligned}$$

The similarity between the combined volumes of phosphorus and bromine is probably accidental. The important point to notice is that the three bromine atoms assume similar volumes to the value in  $\text{R} - \text{Br}$ , which has been shown to be 26·9. This involves a failure of the usual law of increase with the accumulation of halogen atoms about a single carbon atom for some reason or other.

#### *Iodine I.*

The free volume is according to Billet—

$$2[\text{I}] = 2 \times 33\cdot5.$$

Methyl iodide.

$$\begin{array}{r}
 \text{CH}_3\text{I} \quad V_m = 63\cdot9 \\
 \text{CH}_3 \quad 26\cdot0 \\
 \text{I} \quad 37\cdot0 \\
 \hline
 \Sigma_n V_a \quad 63\cdot0 \\
 V_m \quad 63\cdot9 \\
 \hline
 \Delta = + 0\cdot9
 \end{array}$$

This result is in accord with those previously obtained for the other series, and is due to the presence of the methyl group as shown in the following table:—

TABLE XXXIX.

Substance.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$\text{CH}_3 - \text{H}$ . .	38·5	29·6	+8·9
$\text{CH}_3 - \text{Cl}$ .	50·7	47·6	3·1
$\text{CH}_3 - \text{Br}$ .	55·7	53·0	2·7
$\text{CH}_3 - \text{I}$ .	63·9	63·0	0·9

These plus differences are found to diminish with the apparent size of the atoms, etc. They also diminish with the number of  $\text{CH}_2$  groups, and thus they nearly disappear at about the third member of each series.

The monoiodides are :—

TABLE XL.

Compound.	$V_m$ .	Volume of the Hydrocarbon Radicle.	I.	V/W.
$\text{C}_2\text{H}_5\text{I}$ . . .	85.8	48.0	37.8	3.730
$\text{C}_3\text{H}_7\text{I}$ . . .	106.8	70.0	36.8	3.683
$\text{C}_4\text{H}_9\text{I}$ . . .	128.2	92.0	36.2	3.663
$\text{C}_5\text{H}_{11}\text{I}$ . .	151.4	114.1	37.3	3.693
$\text{C}_6\text{H}_5\text{I}$ . . .	130.5	92.8	37.7	
Mean value [I] . . .			37.0	

The average value of iodine is—

$$[\text{I}] = 10[\text{H}] = 37.0,$$

which is a relation enabling us to find the variation in the atomic volumes throughout the series.

TABLE XLI.—VALUES OF V/W IN THE ALKYL IODIDE SERIES.

Substance.	W.	$V_m$ .	V/W.
$\text{CH}_3\text{I}$ . .	17	64.1	3.770
$\text{C}_2\text{H}_5\text{I}$ . .	23	85.8	3.730
$\text{C}_3\text{H}_7\text{I}$ . .	29	106.8	3.683
$\text{C}_4\text{H}_9\text{I}$ . .	35	128.2	3.663
$\text{C}_5\text{H}_{11}\text{I}$ . .	41	151.4	3.693

Several higher compounds have been studied by Döbriner, but the curve is not very regular.

In this series, we note similar characteristics to those for the paraffins.



- (a) A gradually diminishing series of values to—  
 (b) a *minimum* at the fourth or fifth member ;  
 (c) an increasing series of values after this minimum.

A similar result is shown in Table XL, col. 4, so that the nature of the curve indicated by the values of  $V/W$  is the true one.

In dealing with the halogens, we may include an *inorganic series* examined by Prideaux.

HgCl <sub>2</sub> 63·3	HgBr <sub>2</sub> 75·1	HgI <sub>2</sub> 92·8
Hg 18·9	Hg 18·9	Hg 18·9
Cl <sub>2</sub> 44·4	Br <sub>2</sub> 56·0	I 74·0
$\Sigma_n V_a = 63·3$	$\Sigma_n V_a = 74·9$	$\Sigma_n V_a = 92·9$

The values of Cl, Br, and I are—

$$[\text{Cl}] = 22·2 \qquad [\text{Br}] = 28·0 \qquad [\text{I}] = 37·0.$$

in an inorganic series.

These are similar to those already shown for organic compounds.

The average volumes of the halogen atoms are thus—

$V_a$	[F] = 8·7	At. wt. 19·0
	[Cl] = 22·0	„ 35·5
	[Br] = 28·0	„ 80·0
	[I] = 37·0	„ 127·0

In this family the atomic volumes increase with the atomic weights, but not proportionally.

## Constitutive Effects among the Halogen Compounds.

### The Combined Influence of a Halogen Atom and Iso Group.

The effect of the branching of the hydrocarbon chain when halogen atoms are present, has now to be studied.

Among the hydrocarbons (paraffins), a branching of the chain is, so far as we can see, uniformly accompanied by a contraction. If, however, one of the hydrogen atoms be substituted by a halogen atom, a different result ensues. The following table shows this.

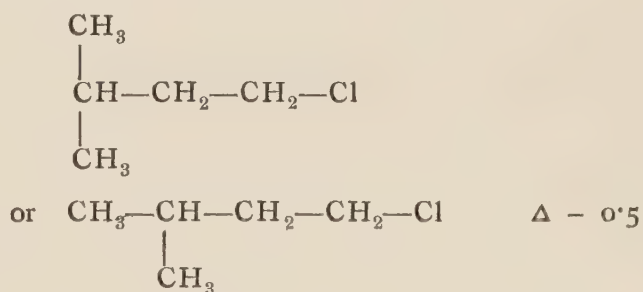
TABLE XLII.

Chlorides.	V <sub>m</sub> .	Δ.	V <sub>m</sub> .	Iso, etc. Compounds.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . Cl . . .	91.7	+2.6	94.3	(CH <sub>3</sub> ) <sub>2</sub> CHCl.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . Cl . .	112.7	+1.8	114.5	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> Cl.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> Cl .	135.3	-0.5	134.8	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> . CH <sub>2</sub> . Cl.
<i>Bromides.</i>				
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . Br . . .	97.3	+2.2	99.5	(CH <sub>3</sub> ) <sub>2</sub> . CHBr.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . Br . .	118.6	+1.0	119.6	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> Br.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> Br	141.2	-0.4	138.8	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> . CH <sub>2</sub> . Br.
<i>Iodides.</i>				
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . I . . .	107.1	+1.5	108.6	(CH <sub>3</sub> ) <sub>2</sub> CHI.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . I . .	128.2	+0.2	128.4	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> . I.
CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> I .	151.4	-0.3	151.1	(CH <sub>3</sub> ) <sub>2</sub> . CH . CH <sub>2</sub> . CH <sub>2</sub> . I.

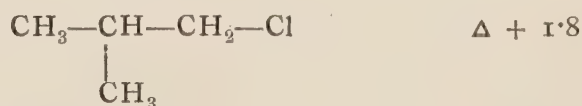
We see that in the case of the propyl and butyl halogen compounds, the iso or branched chain derivatives are larger than those with straight chains. Exceptions to this are found among the amyl compounds, which show contractions approximately equal to that for the iso-group.

The positive differences thus seem to be connected with an approach of the halogen atoms to the iso-group.

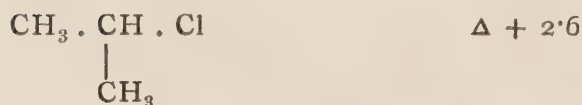
Amyl chloride (iso)



Butyl chloride (iso)



Propyl chloride (iso)

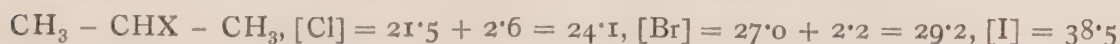


The inference is, that the approximation of a halogen atom to a methyl group causes an *expansion* which diminishes as the two groups become separated, until, when sufficiently removed, the contraction for the iso group alone remains.

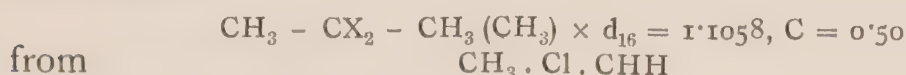
*We have thus to admit the possibility of the interaction of groups not directly connected by valency linkings.*

Whatever be the exact cause of the expansions, it would seem

that they take effect on the halogen atoms, that is, their volumes increase by the values  $\Delta$ . Thus in the compounds



This fact is proved by an examination of the compounds of formula



$$V_m \quad 114.8$$

$$2\text{CH}_3 \quad 52.0$$

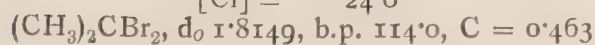
$$C \quad 14.8$$

$$\hline 66.8$$

$$V_m \quad 114.8$$

$$2[\text{Cl}] = \quad 48.0$$

$$[\text{Cl}] = \quad 24.0$$



from



$$V_m \quad 126.4$$

$$V_m \quad 126.4$$

$$(\text{CH}_3)_2\text{C} \quad 66.8$$

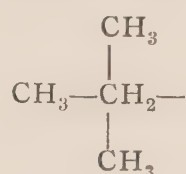
$$\hline 59.6$$

$$2[\text{Br}] = \quad 59.6$$

$$[\text{Br}] = \quad 29.8$$

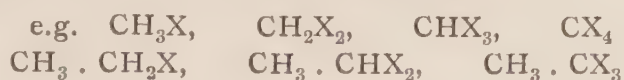
These facts are of the greatest importance. They show that an atom may have more than one value according to its position, in a hydrocarbon chain.

Calculation shows that the above expansions are much augmented in compounds containing the tertiary group—



### $\alpha$ , $\beta$ , and $\gamma$ Halogen Compounds—Partial Rings.

The di- and tri-substituted paraffins in which the halogen atoms are attached to a single carbon atom



have been studied.

In all of these  $\alpha$  compounds the additive rule is approximately realized. Other compounds, however, occur, in which the halogen atoms are attached to different carbon atoms, e.g.  $\text{X} - (\text{CH}_2)_n - \text{Y}$ .

This mode of distribution is found to be accompanied by very considerable modifications in volume.



TABLE XLIII.—POLYHALOGEN COMPOUNDS.

 $\alpha$ ,  $\beta$ , and  $\gamma$  derivatives.

$\alpha$ Compounds.	$V_m$ or $\Sigma_n V_a$ .	$\Delta$ .	$V_m$ .	$\alpha$ , $\beta$ , etc., Compounds.
$\text{CH}_3 \cdot \text{CHCl}_2$ . . .	88.96	-3.6	85.3	$\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{Cl}$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHCl}_2$ .	$\Sigma_n V_a$ 111.0	-3.1	107.9	$\text{CH}_3 \cdot \text{CHCl} \cdot \text{CH}_2\text{Cl}$ .
$\text{CH}_3 \cdot \text{CHBr}_2$ . . .	„ 100.2	-3.1	97.06	$\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$ .
$\text{CH}_3 \cdot \text{CHClH}$ . . .	„ 103.6	-2.6	101.0	$\text{CH}_2\text{Cl} \cdot \text{CH}_2\text{I}$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHBr}_2$ .	„ 122.4	-3.2	119.2	$\text{CH}_3 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ .
$\text{CH}_3 \cdot \text{CCl}_3$ . . .	„ 107.0	-3.3	103.7	$\text{CH}_2\text{Cl} \cdot \text{CHCl}_2$ .
$\text{C}_2\text{H}_4\text{Cl}_4$ . . .	„ 125.4	-6.0	119.4	$\text{CHCl}_2 \cdot \text{CHCl}_2$ .
$\text{C}_2\text{HCl}_5$ . . .	„ 143.8	-5.6	138.2	$\text{CHCl}_2 \cdot \text{CCl}_3$ .
$\text{C}_2\text{Cl}_4$ . . .	„ 118.0	-3.2	114.8	$\text{CCl}_2 : \text{CCl}_2$ .
$\text{C}_2\text{H}_2\text{Br}_2$ . . .	„ 93.0	-1.6	91.4	$\text{CHBr} : \text{CHBr}$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHCl}_2$ .	111.0	-5.0	106.0	$\overset{\alpha\gamma}{\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}}$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHBr}_2$ .	122.4	-4.3	118.1	$\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ .

It is evident from the above that

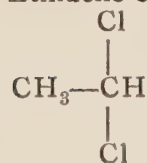
(a) A halogen atom in the ( $\beta$ ) position, counting from the end of the carbon chain, occasions a contraction of 3 units, but only if one or two halogen atoms are found in the ( $\alpha$ ) position. Halogen atoms in the ( $\alpha$ ) position alone or in the ( $\beta$ ) position alone do not cause contractions (*vide ante*).

(b) Given the requisite number in the ( $\alpha$ ) position, the contraction depends upon the number in the ( $\beta$ ) position. This is seen from the fact that in tetrachlor and pentachlor ethane, the contractions are double, or amount to 6.0 units.

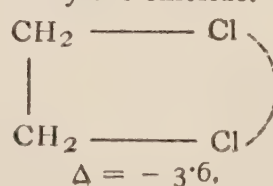
*Conclusion* : The only explanation which we can give to the above facts is, that there is some sort of interaction between the two chlorine atoms, which is due to their being contiguous. This necessitates such an arrangement of the atoms as to allow of this, and the contraction depends upon the number of groups in the partial ring.

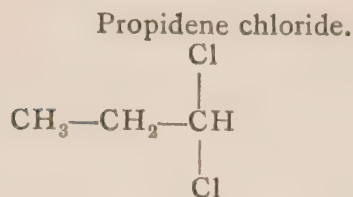
This is shown by means of the plane formulæ as follows :—

Ethidene chloride.

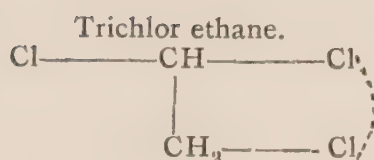
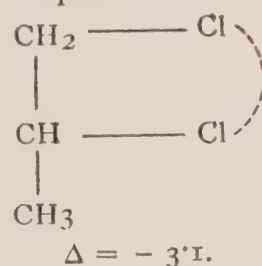


Ethylene chloride.



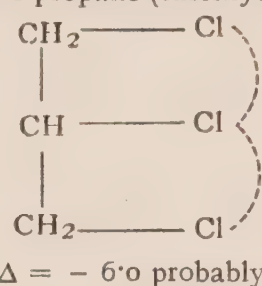


Propidene chloride.

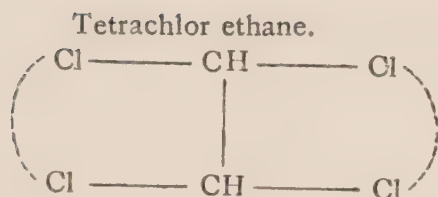


$$\Delta = -3.1.$$

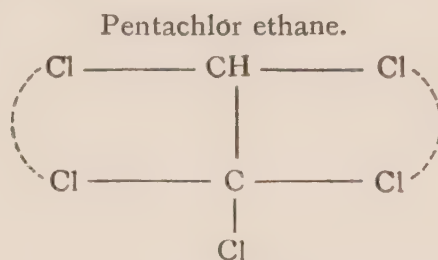
Trichlor propane (chlorhydrin).



See Chapter II, p. 52.



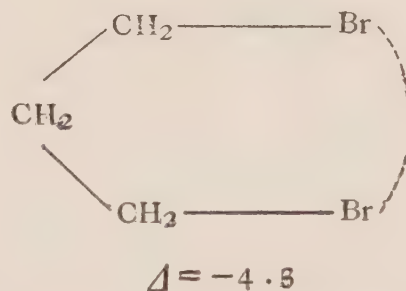
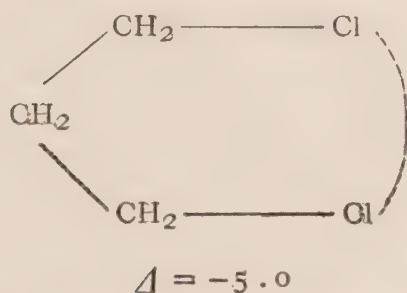
$$\Delta = -6.0.$$



$$\Delta = -5.6$$

(c) If we study the trimethylene derivatives, we find that the contractions are largely increased. Since the removal of a halogen atom to the  $\gamma$  position would separate it from the one in the  $\alpha$  position, and the large contractions indicate a corresponding interaction, we must suppose that the configuration of the hydrocarbon chain is modified in accordance with these results.

This involves an arrangement of the carbon atoms on a curve, or the formation of a *partial ring*.



Although the result is doubtless due to an approximation of the halogen atoms, it seems clear that all the atoms share in the above modification. Probably  $\delta$  and  $\epsilon$  compounds would show still larger contractions.

(d) The presence of an ethenoid linkage influences the amount of the contraction.

It has been shown that in compounds  $\text{CH}_3 \cdot \text{CHX} \cdot \text{CH}_3$  and  $\text{CH}_3 \cdot \text{CX}_2 \cdot \text{CH}_3$ , as compared with  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{X}$  and  $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHX}_2$ , X being halogen atoms, etc., the volumes of these atoms are larger in the  $\beta$  position than in the  $\alpha$ . It follows that if there is a contraction when one appears in the  $\alpha$  and also one in the  $\beta$  or  $\gamma$  positions, it must be due to some relation between these contiguous atoms.

Since in the  $\alpha\gamma$  compounds, the contractions are greater than in the  $\beta$ , that is, when they are farther removed, the large contractions can only be attributed to a change in the configuration of the hydrocarbon chain brought about by the interaction of the terminal atoms.

### The Volumes of the Unsaturated Polyhalogen Compounds.

There are evidences that on passing from the saturated to the unsaturated polymethylenes, a constitutive change takes place, which is connected with the combined influence of the olefin link and the halogen atoms. Only one or two data, however, exist, so that it is scarcely possible to obtain that extent of view which leads us to certain conclusions. It will be thus necessary to resort to calculation to supply the deficiency to some extent.

#### Chlorides.

Ethyl chloride  $V_m$ .  
 $\text{CH}_3\text{—CH}_2\text{Cl}$  71.7

Ethylidene chloride.  
 $\text{CH}_3\text{—CHCl}_2$  88.9 (obs.)  
 $C = 0.46$  89.0 (by form.)

$$\Delta = 8.9 \text{ for } \text{H}_2$$

Ethylene chloride.  
 $\text{CH}_2\text{Cl—CHCl}$  85.3 (obs.)  
 $C = 0.46$  85.6 (by form.)

Acetylene tetrachloride.  
 $\text{CHCl}_2\text{—CHCl}_2$  —  
 120.6 (by form.)

$$\Delta = 5.6 \text{ for } \text{H}_2$$

Propylene chloride.  
 $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{Cl}$  91.7

$$\Delta = 6.7 \text{ for } \text{H}_2$$

Vinyl chloride  $V_m$ .  
 $\text{CH}_2 = \text{CHCl}$  —

Unsymm. dichlorethylene.  
 $\text{CH}_2 = \text{CCl}_2$  79.9 (obs.)  
 80.1 (by form.)

Symm. dichlorethylene.  
 $\text{CHCl} = \text{CHCl}$  —

Tetrachlorethylene.  
 $\text{CCl}_2 = \text{CCl}_2$  114.8 (obs.)  
 115.0 (by form.)

Allyl chloride.  
 $\text{CH}_2 = \text{CH—CH}_2\text{Cl}$  85.0



*Bromides.*

Ethyl bromide $V_m$ . $\text{CH}_3\text{—CH}_2\text{Br}$ 77·1 (by obs.)	$\Delta = 5·8$ for $\text{H}_2$	Vinyl bromide $V_m$ . $\text{CH}_2 = \text{CHBr}$ 71·3
Ethylene bromide. $\text{CH}_3\text{—CHBr}_2$ —	98·8 (by form.) $\Delta = 5·8$ for $\text{H}_2$	Unsymm. dibromethylene. $\text{CH}_2 = \text{CBr}_2$ —
Ethylene bromide. $\text{CH}_2\text{Br—CH}_2\text{Br}$ 97·1 (obs.) 97·1 (by form.)	$\Delta = 5·8$ for $\text{H}_2$	Symm. dibromethylene. $\text{CHBr} = \text{CHBr}$ 91·4 (obs.) 91·3 (by form.)
Tribromomethane. $\text{CH}_2\text{Br—CHBr}_2$ —	119·3 (by form.) $\Delta = 5·7$ for $\text{H}_2$	Tribromethylene. $\text{CHBr} = \text{CBr}_2$ —
Propylene bromide. $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{Br}$ 97·3 (obs.)	$\Delta = 6·5$	Allylene bromide. $\text{CH}_2 = \text{CH—CH}_2\text{Br}$ 90·8 (obs.)

In the above table, we have a summary of the results for the unsaturated polyhalides. We find in the derivatives of ethane a difference of 5·7 for  $\text{H}_2$ .

normal $\Delta$ for $\text{H}_2$	7·4
actual $\Delta$ for $\text{H}_2$	5·8
change in value	<u>1·6</u>

From this we conclude that there is an increase of 1·6 in the volume of the unsaturated compound, presumably owing to the close association of the halogen atom or atoms with the olefin links  $|\equiv|$

## Acetylene tetrachloride.

$\text{Cl—C—Cl}$ $\parallel$ $\text{Cl—C—Cl}$	$\text{CCl}_2 = \text{CCl}_2$
	2 [C] = 29·6
	4 [Cl] = 88·8
	<u>118·4</u>
for part. ring	5·2
	<u>113·2</u>
for unsat.	+ 1·6
	<u>114·8</u>
	$\Sigma_n V_a$ 114·8
	$V_m$ 114·8

## Vinyl bromide.

$\text{CH}_2 = \text{CHBr}$	
$\text{CH}_3\text{—CH}_2\text{Br}$ 77·1	
less 2H	7·4
	<u>69·7</u>
for unsat.	+ 1·6
	<u>71·3</u>
$\Sigma_n V_a$	71·3
$V_m$	<u>71·3</u>

## Unsymm. dibromethylene.

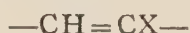
$\text{CH}_2 = \text{CBr}_2$	
$\text{Br—CH}_2\text{—CH}_2\text{Br}$ 98·8	
$\text{CH}_2 = \text{C}$ $\mid$ $\text{Br}$	less $\text{H}_2$ 7·4
	<u>91·4</u>
	for unsat. + 1·6
	<u>93·0</u>
$\Sigma_n V_a$	93·0
$V_m$	<u>93·0</u>

Symm. dibromethylene. CHBr = CHBr			Tribromethylene. CHBr = CBr <sub>2</sub>		
CH—Br			Br—C—Br	2C	29·6
$\parallel$	2CH	37·0	$\parallel$	H	3·7
CH—Br	2Br	56·0	CH—Br	3Br	84
		<hr/>			<hr/>
		93·0			117·3
for part. ring	—	3·2	for part. ring	—	3·2
		<hr/>			<hr/>
		89·8			114·1
for unsat.		+ 1·6	for unsat.		+ 1·6
		<hr/>			<hr/>
$\Sigma_n V_a$		91·4	$\Sigma_n V_a$		115·6
$V_m$		91·4	$V_m$		113·6
		<hr/>			<hr/>
			or better		
			Tribromethane		
			CH <sub>2</sub> Br—CHBr <sub>2</sub>		119·3
			less 2H		— 7·4
					<hr/>
					111·9
			for unsat.		+ 1·6
					<hr/>
			$\Sigma_n V_a =$		113·5
			$V =$		113·6
					<hr/>

The following show scarcely any effect for unsaturation :—

Allyl chloride. CH <sub>2</sub> = CH—CH <sub>2</sub> Cl			Allyl bromide. CH <sub>2</sub> = CH—CH <sub>2</sub> Br		
C <sub>3</sub> H <sub>5</sub>		62·9	C <sub>3</sub> H <sub>5</sub>		62·9
Cl		22·1	Br		28·0
		<hr/>			<hr/>
$\Sigma_n V_a =$		85·0	$\Sigma_n V_a =$		90·9
$V_m =$		85·0	$V_m =$		90·8
		<hr/>			<hr/>

From the above, we conclude, that, in the unsaturated group

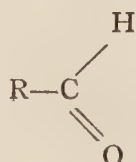


where X is a negative atom like Cl, Br, etc., there is an expansion of + 1·6. Since this expansion remains the same whatever be the number of halogen atoms present, we are probably right in connecting it with the presence of the olefin linkage  $|\equiv|$ .

In allyl chloride, for example, such a feature is not noticed. This shows that if the halogen atom be sufficiently separated from the olefin link no expansion occurs.

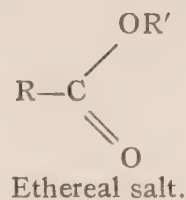
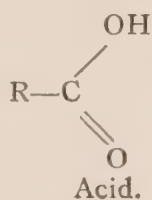
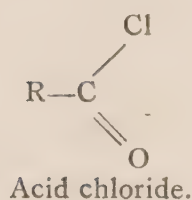
In considering this explanation, we are led to find in it a reason for a somewhat similar phenomenon connected with the  $-\text{C}=\text{O}$  group.

In the aldehydes,



we shall find that the volume of O'' is 7.4 (Chap. IV.), but in certain other compounds, which involve the substitution of hydrogen by chlorine, hydroxyl, and other negative groups, we find a considerable expansion.

Thus in—



the volume of O'' is 11.1, so that there is an expansion of + 3.7 as compared with O'' in the aldehydes. Again we notice that similarly there is unsaturation in the C=O group, as in the —C=C— group.

We may thus suppose that these expansions are due to a similar cause in the two cases. It is, moreover, not improbable that certain well marked variations in the atomic volumes of certain elements, which like oxygen show two or more values, may also be due to the co-existence of unsaturation and negative groups.

It must be observed that unsymmetrical dichlorethylene



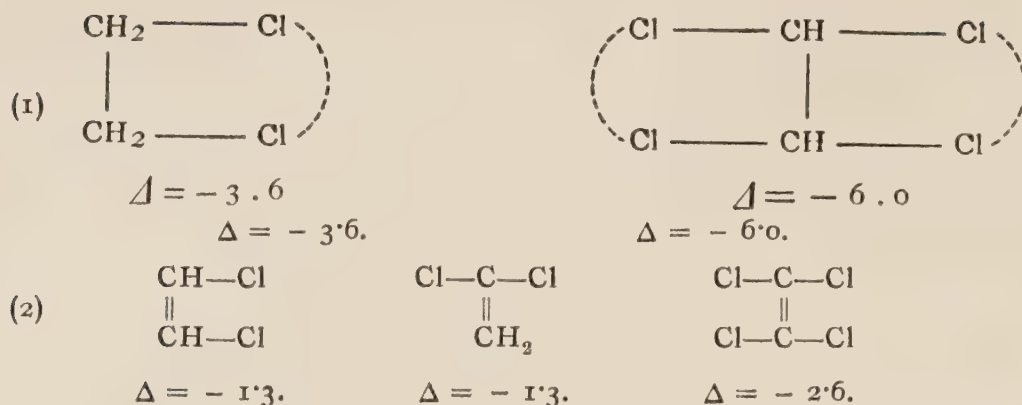
is exceptional, in that there is a contraction instead of an expansion.\* We do not propose at present to do more than record the fact, as it is evident that we need much more varied and numerous data before we can deal adequately with the subject or come to certain conclusions. It is possible that a repetition of the determination of the volume of unsymmetrical dichlor ethylene and the determination of the volume of symmetrical dichlor ethylene might show different results.

#### *General Remarks on Saturated and Unsaturated Polyhalogen Compounds.*

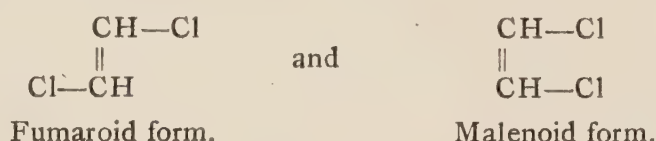
The following represents a comparison of the contractions in saturated and unsaturated derivatives.

\* This seems to be due to the fact that the CH<sub>3</sub> group in CH<sub>3</sub>.CHCl<sub>2</sub> is unusually large.





In regard to (2), we must also note the possible existence of geometrical isomers, so that we might have



Precisely how these differ as regards volume is not quite certain at present, but there is evidently here a rich field for future research.

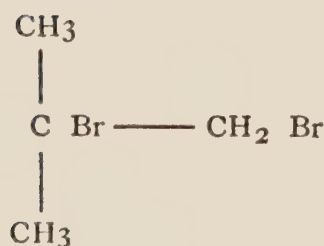
Applications of the above principles to a study of more complex compounds are indicated by the following.

We have noticed the following effects.

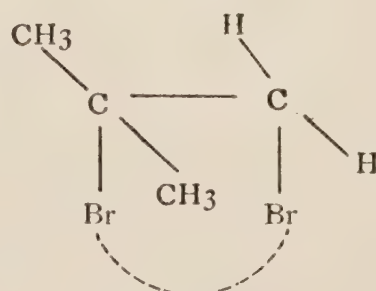
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}-\text{Cl} \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{C}_3\text{H}_7 \\   \\ \text{Cl} \end{array}$	$\begin{array}{r} 70.0 \\ 22.1 \\ \hline 92.1 \\ 94.6 \\ \hline \Delta \quad + 2.5 \\ \hline \hline \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}-\text{Br} \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{C}_3\text{H}_7 \\   \\ \text{Br} \end{array}$	$\begin{array}{r} 70.0 \\ 28.0 \\ \hline 98.0 \\ 99.5 \\ \hline \Delta = +1.5 \\ \hline \hline \end{array}$
--	---	--	--	---	---

Thorpe<sup>32</sup> has given a volume of  $V_m = 142.6$  to the following compound.

Isobutylene bromide.



or



$C_4H_8$	$4 \times 22.1$	88.4	or	$2 CH_3$	52.0
	$2Br$	56.0		$\quad C$	14.8
	$\Sigma_n V_a$	144.4		$CH_2$	22.1
less iso group		- 0.5		$Br'$	28.0†
				$Br''$	29.2†
		143.9			
Br atom and iso group		+ 2.0*			146.1
					- 3.1
		145.9			
For partial ring		- 3.1			143.0
				iso struct.	- 0.5
	$\Sigma_n V_a$	142.8			
	$V_m$	142.6			142.5

TABLE XLIV.—AROMATIC HALOGEN COMPOUNDS.

Substance.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$C_6H_5F$ .	101.6	116.0	- 14.4
$C_6H_5Cl$ .	114.6	129.1	- 14.5
$C_6H_5Br$ .	120.0	135.3	- 15.3
$C_6H_5I$ .	130.7	144.3	- 13.6
Mean value .			- 14.5

There is associated with these compounds the normal contraction of - 14.5 for the ring, from which it follows that the volumes of chlorine, bromine, and iodine are not very different from their volumes in paraffin derivatives.

The volume of—

$$C_6H_5- \text{ is } 96.0 - 3.2 = 92.8$$

$$\text{and of } C_6H_4= \text{ is } 96.0 - 2 \times 3.2 = 89.6.$$

The halogens in these aromatic compounds can be shown to have nearly the same volumes as in the aliphatic compounds  $R - X$

$$Cl = 114.6 - 92.8 = 21.8$$

$$Br = 120.0 - 92.8 = 27.2$$

$$I = 130.7 - 92.8 = 37.9$$

In open-chain compounds

$$Cl = 21.5$$

$$Br = 27.0$$

$$I = 37.0$$

\* The value of  $\Delta$  found was 1.5 for association of Br and iso group. The value of - 0.5 for the iso group should be added, so that the full value for the former constitutive influence is + 2.0.

† See Table XLII. The volumes of the bromine atoms are taken as  $[Br] = 27.0 + \Delta$ .

There is, however, indication of a slight increase from Cl to I, possibly due to the unsaturation of benzene.

TABLE XLV.—OTHER AROMATIC HALOGEN COMPOUNDS.

Substance.	$V_m$ .	$\Sigma_n V_a - R$ .	$\Delta$ .
1 : 4 $C_6H_4(CH_3)Cl$ .	135.3	137.3	-2.0
$C_6H_5 \cdot CH_2Cl$ .	133.8	136.5	-2.7
$C_6H_5 \cdot CHCl_2$ .	154.7	154.6	—
1 : 2 $C_6H_4(CH_3)Br$ .	142.1	142.7	—

Some of these results are unusual, since *o* compounds usually possess contractions and *p* compounds do not, but the data are not sufficient to enable us to account for them. Compounds of the type of *o*, *m*, and *p* dihalogen benzene derivatives have not yet received attention.

### The Gradual Chlorination of the Benzene Molecule.

This very interesting question can be studied owing to the work of Jungfleisch.<sup>33</sup>

The volume of  $C_6H_6$  is 96.0, and every atom of hydrogen subtracted involves a loss in volume of 3.2.



Monochlorobenzene,  $C_6H_5Cl$ .  $V_m$  114.6 b.p. 132

(Unsymmetrical or odd)

$$Cl = C_6H_5Cl - C_6H_5 = 114.6 - 92.8 = 21.8.$$



1 : 4 Dichlorobenzene,  $C_6H_4Cl_2$ .  $V_m$  130.9 b.p. 172

(Symmetrical or even)

$$Cl_2 = 130.9 - 89.6 = 41.3.$$

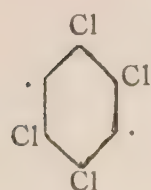


1 : 2 : 4 Trichlorobenzene,  $C_6H_3Cl_3$ .  $V_m$  149.1 b.p. 213

(Unsymmetrical or odd)

$$Cl_3 = 149.1 - 86.4 = 62.7.$$

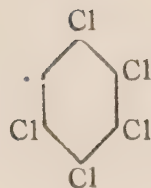




1 : 2 : 4 : 5 Tetrachlorobenzene,  $C_6H_2Cl_4$ ,  $V_m$  164·8 b.p. 244

(Symmetrical or even)

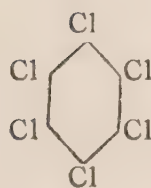
$$Cl_4 = 164\cdot8 - 83\cdot2 = 81\cdot6.$$



1 : 2 : 3 : 4 : 5 Pentachlorobenzene,  $C_6HCl_5$ ,  $V_m$  183·9 b.p. 276

(Unsymmetrical or odd)

$$Cl_5 = 183\cdot9 - 80\cdot0 = 103\cdot9.$$



Hexachlorobenzene,  $C_6Cl_6$ ,  $V_m$  200·0 b.p. 326

(Symmetrical or even)

$$Cl_6 = 200\cdot0 - 76\cdot8 = 123\cdot2.$$

The average volume of chlorine is 20·0 in all the compounds. A close study of the results, however, shows that the chlorine atoms are not equal in volume, but that each pair involves a loss of about 2·3 or 2·5.<sup>34</sup>

TABLE XLVI.

Substance.		$V_x Cl$ .	$\Delta$ .	
Monochlorobenzene	$C_6H_5Cl$	21·8		(Unsymm. or odd).
<i>p</i> -Dichlorobenzene	$C_6H_4Cl_2$	41·3	19·5	(Symm. or even).
Trichlorobenzene	$C_6H_3Cl_3$	62·7	21·4	(Unsymm. or odd).
Tetrachlorobenzene	$C_6H_2Cl_4$	81·6	18·9	(Symm. or even).
Pentachlorobenzene	$C_6HCl_5$	103·9	22·3	(Unsymm. or odd).
Hexachlorobenzene	$C_6Cl_6$	123·2	19·3	(Symm. or even).

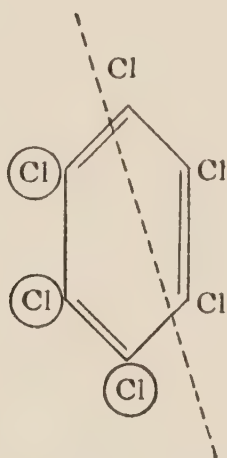
There is thus a distinction between the Cl atom on one side of the molecule, and the Cl atom in the para position with reference to it, or the two atoms on opposite sides of the ring involve a contraction of 2·6 on the average.

Thus we have

TABLE XLVII.

	Normal.	Abnormal.
1st Chlorine $Cl^i$	21·8	—
2nd Chlorine $Cl^{ii}$	—	19·5
3rd Chlorine $Cl^{iii}$	21·4	—
4th Chlorine $Cl^{iv}$	—	18·9
5th Chlorine $Cl^v$	22·3	—
6th Chlorine $Cl^{vi}$	—	19·3
Mean values	<u>21·8</u>	<u>19·2</u>
	$\Delta = 2\cdot6$	

The smaller values apply to the chlorine atoms marked (Cl) in the following diagram.



and the apparent result is that one-half of the chlorine atoms differ from the other half.

## CHAPTER IV.

### THE MOLECULAR VOLUMES OF ORGANIC COMPOUNDS CONTAINING OXYGEN.

#### The Volumes of Oxygen.

KOPP (loc. cit.) recognized the existence of two different values for oxygen—

Hydroxyl O'	7.8
Carboxyl O''	12.2.

The numbers are not very different from those now advocated, but it is necessary frequently to suppose that the volume of oxygen is not always one of those just indicated. Owing perhaps to constitutive influences several other values are also found necessary.

The volume of *free oxygen* at the boiling-point is, according to Olszewski, Ber. 17 ref. 198, about 14.0 density (1.110 to 1.137).

$$V \text{ (O : O)} = 28.0.$$

From the critical data,

$$T_C = 155. \quad P_C = 50 \text{ atmos.} \quad \text{b.p.} = 92,$$

we find by D. Berthelot's formula—

$$V = \frac{M}{D} = \frac{11.1 T_C^2}{P_C(2P_C - T)} = 24.4 \text{ for O}_2.$$

The atomic volume of free oxygen will be found to be greater than that of any of its combined values.

#### Compounds of Oxygen.

Among the simple compounds of oxygen is *water* H<sub>2</sub>O, which, contrary to expectation, finds its place at the head of the symmetrical ether series.

$$\begin{array}{lcl} \text{H} - \text{O} - \text{H} & & \text{CH}_3 - \text{O} - \text{CH}_3 \\ V_m(\text{H}_2\text{O}) = 18.9 & & [\text{O}] = 18.9 - 2 \times 3.7 = 11.5 \\ \text{Hydrogen dioxide } \text{H} - \text{O} \equiv \text{O} - \text{H} & & V_m = 23.4 \\ 2[\text{O}^{\text{iv}}] = 23.4 - 7.4 = 16.0. \\ \text{Thus } [\text{O}^{\text{iv}}] = 8.0, \end{array}$$



This compound seems to contain two hydroxyl groups—a fact which is deduced from the diminished volume of oxygen.

A similar diminution is also seen in the alcohol series.

TABLE XLVIII.—THE ALCOHOLS  $C_nH_{2n+1}O$ . See Le Bas, Ref.<sup>35</sup>

Compound.	$V_m$ .	$\Delta$ .	$V_m$ .	The paraffins.
$C_3H_7OH$ . .	81.4	7.4	74.0	$C_3H_8$ .
$C_4H_9OH$ . .	102.1	6.1	96.0	$C_4H_{10}$ .
$C_5H_{11}OH$ . .	123.7	5.9	117.8	$C_5H_{12}$ .
$C_6H_{13}OH$ . .	146.4	6.5	139.9	$C_6H_{14}$ .
$C_7H_{15}OH$ . .	168.7	6.1	162.6	$C_7H_{16}$ .
Mean . . .		6.4		

The volumes of the simple compounds methyl and ethyl alcohols are somewhat different from the volumes they would possess, if they were strictly comparable with the succeeding members of the series. This feature seems to be common to all homologous series both in the case of molecular volumes and for numerous other physical properties also.

Alcohol.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$CH_3 \cdot OH$	42.8	36.0	+ 6.8
$C_2H_5 \cdot OH$	62.1	58.2	+ 3.9
$C_3H_7 \cdot OH$	81.4	81.4	—

The effect of adding the group  $CH_2$  a number of times, is similar to that observed when progressively large atoms like H, Cl, Br, and I are added to the radicle  $CH_3$ , as already shown.

This effect, in a wide sense, may be considered to be due to differences in complexity, or to increase in volume, and it probably indicates the existence of differences between the internal forces of affinity in the different compounds. At any rate it shows that there are such differences in the distribution of force in the various compounds, that they are not strictly comparable at the boiling-point. These features represent slight differences in constitution existing.

We have supposed that the relation

$$[C] = 4[H]$$

holds in the paraffin series.

So there is every reason to suppose that the relation

$$[O'] = 2[H]$$

is true in the alcohol series. The evidence is as follows:—

$$\text{Propyl alcohol } C_3H_7OH \quad 81.46 = 11 \times 7.405$$

$$\text{Allyl } \quad \quad \quad C_3H_5OH \quad 74.08 = 10 \times 7.408$$

$$\Delta \text{ for } H_2 = 7.38$$

If we consider  $2[H]$  to represent a volume of 7.4, then hydroxyl oxygen also possesses this volume.

Whether this is exactly so or not, the utilization of this relation enables us to find the variation in the atomic volumes in series of compounds like that of the alcohols. In calculations it is better to use the value  $[O'] = 6.4$ .

### The Branched Hydrocarbon Chain.

TABLE XLIX.

Normal Compounds.	$V_m$ .	$\Delta$ .	$V_m$ .	Branched Chain Compounds.
$CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$	81.46 (Sch.)	-0.54	80.92 (Sch.)	$\left. \begin{matrix} CH_3 \\ CH_3 \end{matrix} \right\} CH(OH).$
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	101.79 (Sch.)	+0.49	82.97 (Z)	$\left. \begin{matrix} CH_3 \\ CH_3 \end{matrix} \right\} CH \cdot CH_2(OH).$
	102.11 (Z)	—	101.86 (Sch.)	$\left. \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} \right\} C(OH).$
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$	123.6 (Z)	+1.00	102.8 (Th.)	$\left. \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} \right\} CH \cdot (CH_2)_2OH.$
		-0.50	123.1 (Sch.)	$\left. \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} \right\} C \cdot (OH)CH_2 \cdot CH_3.$
			123.6 (Th.)	$\left. \begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} \right\} CH \cdot CH_2OH.$
		-2.20	121.4 (Th.)	$\left. \begin{matrix} CH_3 \\ CH_3 \cdot CH_2 \end{matrix} \right\} CH \cdot CH_2OH.$
$CH_3 \cdot (CH_2)_6 \cdot CH_2(OH)$	190.9 (Z)	-1.60	122.0 (Th.)	$\left. \begin{matrix} CH_3 \\ CH_3 \cdot CH_2 \end{matrix} \right\} CH \cdot CH_2OH.$
		+0.6	191.5 (Sch.)	$\left. \begin{matrix} CH_3 \\ CH_3 \cdot CH(OH)C_6H_{13} \end{matrix} \right\}$

These results are most contradictory, a fact which is rendered more evident by the observation that the data due to different observers sometimes show positive, and sometimes negative differences.

It follows, that no general rules can be drawn up which would indicate the connexion between these differences and the position

of the OH group in the chain, or its position relative to the iso group.

It is at present difficult to understand the reason for such differences.

The butyl alcohols of Thorpe indicate a close relationship between the position of the (OH) group and that of the iso group.

In these instances we are able to state that the minus difference is greater the nearer the (OH) group is to the iso group.

The following consideration emphasizes the difficulties attending a satisfactory explanation of the above results. This is, that there are possibly three overlapping constitutive effects which, moreover, may not be quite independent:—

- (a) The effect of the branched chain.
- (b) The position and influence of the (OH) group.
- (c) The influence of the (OH) group on the iso group.

A re-determination of all the values by one observer, and a more extended body of data would doubtless clear up these difficulties.

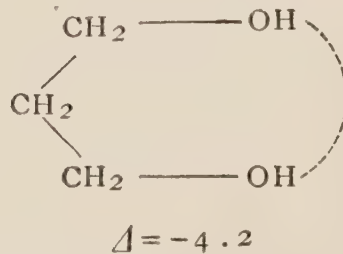
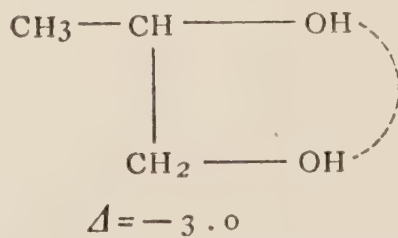
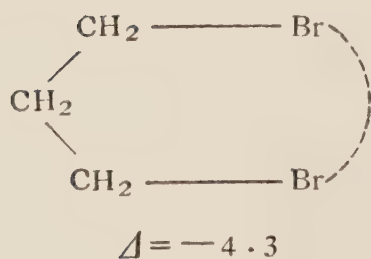
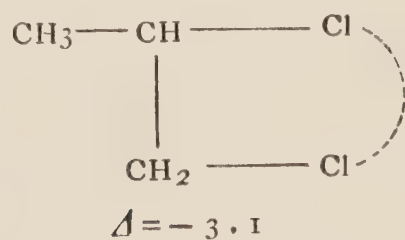
### Partial or Incomplete Rings.<sup>36</sup>

#### $\alpha\beta$ and $\alpha\gamma$ Compounds.

TABLE L.

	Compound.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
Ethylene	Glycol $\text{CH}_2(\text{OH}) \cdot \text{CH}_2(\text{OH})$	64.9*	66.4	-1.5
Propylene	„ $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2(\text{OH})$	85.4	88.4	-3.0
Trimethylene	„ $\text{CH}_2(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2(\text{OH})$	84.2	„	-4.2

These compounds are analogous to the  $\alpha\beta$  and  $\alpha\gamma$  halogen compounds, and the values of  $\Delta$  are:—



\* This value due to Ramsay is probably too large, thus making the value of  $\Delta$  too small.



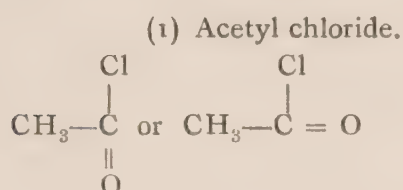
The contractions are thus due to particular configurations of the molecules which have been already noticed. They have been named partial or incomplete rings.

The following conclusions are drawn :—

(a) The  $a\beta$  are smaller than the  $aa'$  compounds by about 3 units.

(b) The  $a\gamma$  are still smaller than the  $aa'$  compounds by about 4 units.

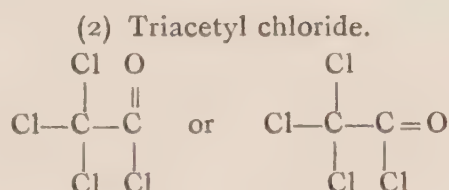
The following compounds show how the atom :O contrasts with the halogens, and with the (OH) group in respect of its effect in the direction indicated.



$V_m$  74.0 (Thorpe).<sup>87</sup>

CH <sub>3</sub>	26.0
C	14.8
Cl	22.1
: O	11.0

$\Sigma_n V_a$  73.9



$V_m$  125.5 (Thorpe).

2C	29.6
4Cl	88.4
: O	11.0

$\Sigma_n V_a$  129.0

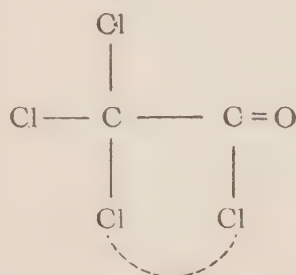
$V_m$  125.5

$\Delta$  -3.5

We see that the atom :O in opposition with a halogen atom does not produce the constitutive effect indicated, but that two halogens in opposition are capable of doing so.

It is evident that in triacetyl chloride we have two adjacent chlorine atoms which produce the normal contraction. The association of the atom :O with Cl does not produce any very appreciable contraction, either owing to the small attraction between the two atoms, or because the double linking of the oxygen causes it to lack mobility.

The formula for the compound in consequence might be—

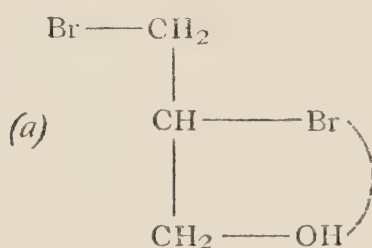


(3) Weger<sup>38</sup> has studied the volume of an  $\alpha\beta$  compound of the same nature.

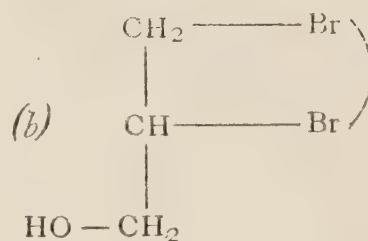
$\alpha\beta$  dibromopropyl alcohol  $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{CH}_2\text{OH}$ .

b.p. $219^\circ$	$V_m$ 124.3.
Volume of $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2(\text{OH})$	81.5
less $\text{H}_2$	-7.4
	<hr/>
plus 2 Br	74.1
	56.6
	<hr/>
$\Sigma_n V_a$	130.7
$V_m$	124.3
	<hr/>
$\Delta$	-6.4
	<hr/>

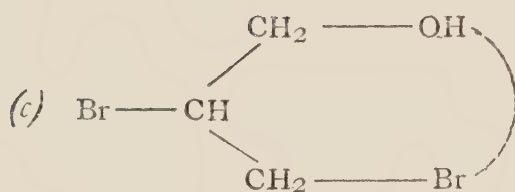
The formulæ which might conceivably apply are:—



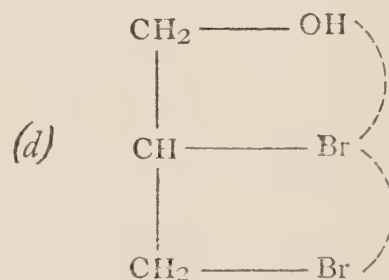
$$\Delta = -3.0$$



$$-3.0$$



$$\Delta = -4.5$$



$$-6.0 \text{ probably}$$

The first two, and possibly the third, are excluded by reason of the magnitude of the contraction. Compounds of the type expressed by the fourth formula have not been directly studied. These include the trichlor, brom hydrins. In order to ascertain the contractions to which these are subject, their volumes may be calculated by the formula already given.

Weger gives for  $\alpha\beta$  dibromopropyl alcohol.  $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br} \cdot \text{CH}_2\text{OH}$ .

$d_0$  2.1682      b.p.  $219^\circ$

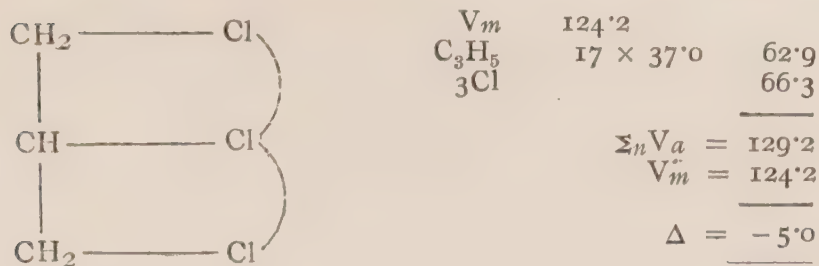
$d_{219}$  1.7535

Thus  $C = 0.532$ .

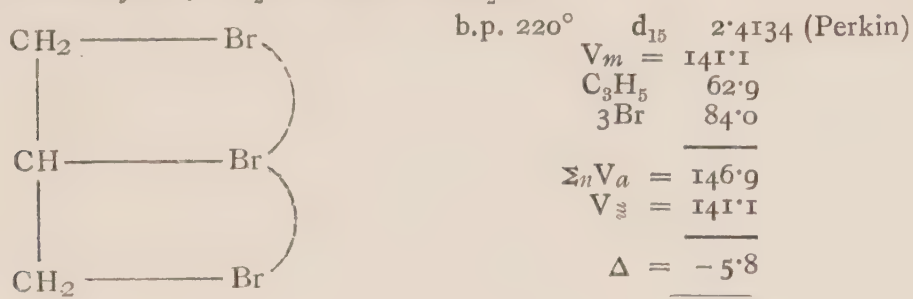
For trichlorhydrin,  $\text{CH}_2\text{Cl} \cdot \text{CHCl} \cdot \text{CH}_2\text{Cl}$

we find  $d_{15}$  1.3980 (Perkin)      b.p.  $156.0$ .

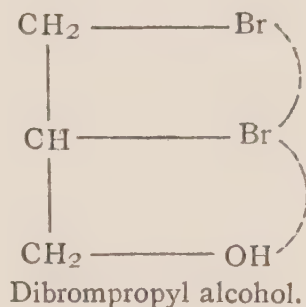
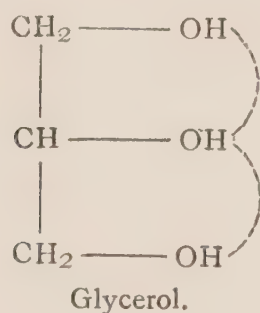
Assuming the value  $C = 0.532$ , we find



For tribromhydrin,  $\text{CH}_2\text{Br} - \text{CHBr} - \text{CH}_2\text{Br}$ .



These trihydrins are evidently similarly constituted to the parent compound glycerol, and we are thus led to suppose that Weger's compound possesses a similar constitution, by reason of its contraction.



A few more of these compounds may now be studied.

$\alpha$  dichlorhydrin  $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Cl}$   
 $\text{C}_3\text{H}_6\text{Cl}_2\text{O}$   $d_{19} 1.367$   $\text{b.p. } 174^\circ$   $C = 0.535$   
 $V_m = 112.7$

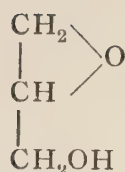


The  $\beta$  dichlorhydrin  $\text{CH}_2(\text{OH}) \cdot \text{CHCl} \cdot \text{CH}_2\text{Cl}$  has a slightly larger volume 113.5, from which we obtain the difference  $\Delta = -5.1$ .



Glycide – epihydrin alcohol  $C_3H_6O_2$ .

The value of C from epichlorohydrin is 0.46.



$$d_0 \ 1.165 \quad \text{b.p. } 162^\circ \quad V_m = 74.4$$

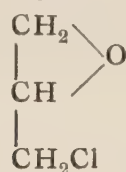
$$\begin{array}{r}
 3\text{CH}_2 \quad 66.6 \\
 2\text{O} \quad 14.8 \quad (2 \times 7.4) \\
 \hline
 \end{array}$$

$$\begin{array}{r}
 \Sigma_n V_a \quad 81.4 \\
 \text{By form.} \quad 74.4 \\
 \hline
 \end{array}$$

$$\Delta \text{ for ring} = \underline{\underline{-7.0}}$$

A compound of this type has been directly investigated.

Epichlorohydrin.



$$V_m = 87.3 \text{ (Thorpe)}$$

$$\begin{array}{r}
 \text{C}_3\text{H}_5 \quad 63.0 \\
 \text{Cl} \quad 22.2 \\
 \text{O} \quad 7.4 \\
 \hline
 \end{array}$$

$$\begin{array}{r}
 \Sigma_n V_a = 92.6 \\
 \text{By Obs.} = 87.3 \\
 \hline
 \end{array}$$

$$\Delta \text{ for ring} = \underline{\underline{-5.3}}$$

These two compounds thus possess three-membered rings.

It thus happens that the value of  $\Delta$  for these ring compounds is similar to those which are constituted the same as glycerol. This is probably a coincidence only. It is, however, possible that part of this value may be due to the attachment of the group  $\text{CH}_2\text{Cl}$  to the ring, since a contraction occurs in the compound  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  for this reason.

In conclusion we see from a study of their molecular volumes that the compounds have without doubt the formulæ which have been given to them.

### Aromatic Compounds.

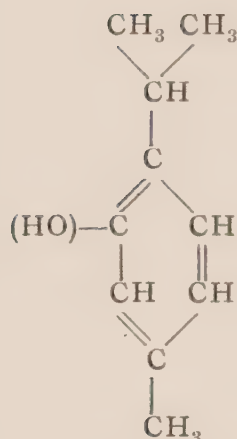
TABLE LI.—THE PHENOLS.

Compounds.	$V_m$ .	$\Delta$ .	$V_m$ .	The Hydrocarbons.
$\text{C}_6\text{H}_5\text{OH}$ . . .	101.9	5.9	96.0	$\text{C}_6\text{H}_6$ Benzene.
$p\text{C}_6\text{H}_4(\text{CH}_3)(\text{OH})$ . .	123.8	5.6	118.2	$\text{C}_6\text{H}_5(\text{CH}_3)$ Toluene.
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . . .	123.7	5.5	„	„
Mean = 5.6				

The volume of  $-O-$  in the phenols is on the average 5.6, and thus is  $6.4 - 5.6 = 0.8$  of a unit smaller than in ordinary alcohols.

This difference indicates the existence of a special constitutive effect caused by the substitution of the aromatic nucleus for the alkyl group R, when the group (OH) is present. For  $C_{10}H_{14}O$  two values are given.

- (a) Ordinary thymol  $V_m$  189.3 (Pinette).  
 (b) Carvol (unspecified) 190.7 (Schiff).



From the formula, which is that of thymol, we get the following calculated volume:—

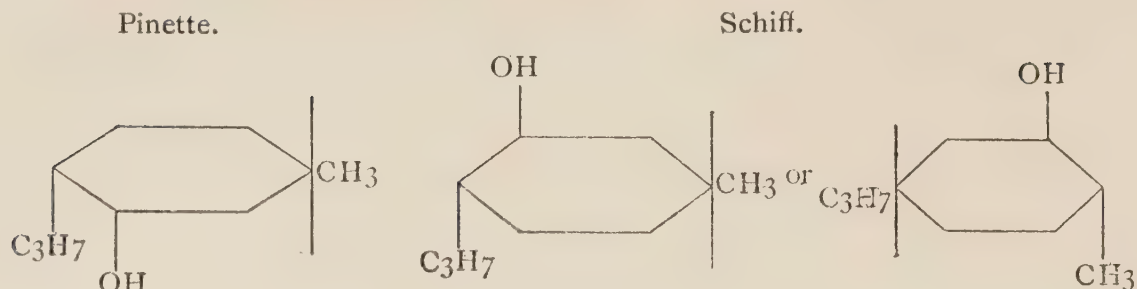
Cymene	$C_{10}H_{14}$	184.6
	less H	- 3.2
		<hr/>
		181.4
	plus OH	9.3 (5.6 + 3.7)
		<hr/>
	$\Sigma_n V_a$	<u>190.7</u>

This is exactly the value given by Schiff. It will be seen, however, that the (OH) group occupies the ortho position with reference to the isopropyl group, and this should occasion a contraction of about 2 units. The normal volume thus is 188.7 approximately, which is similar to the volume given by Pinette.

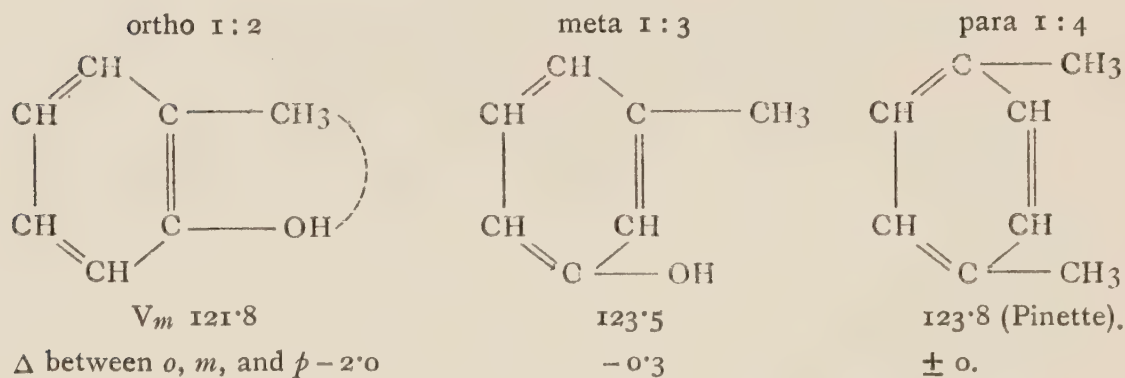
Moreover any other compound of formula  $C_{10}H_{14}O$  would still be subject to a similar contraction, for an OH group in the nucleus would necessarily occupy the ortho position with reference to either the  $C_3H_7$  or the OH group. Thus the volume of any of these compounds would be in the neighbourhood of 189.0.

There is no reason to suppose that Schiff's value is due to experimental error, so that we are compelled to find some other reason for the larger volume.

Remembering that the latter corresponds to a compound in which the paraffin and hydroxyl groups are independent, that is to  $\Sigma_n V_a$ , only allowing for ring structure, we see that the explanation may lie in the fact that the groups are opposed. The structure of Pinette's compound would be "adjacent".



If we compare the cresols, we find—

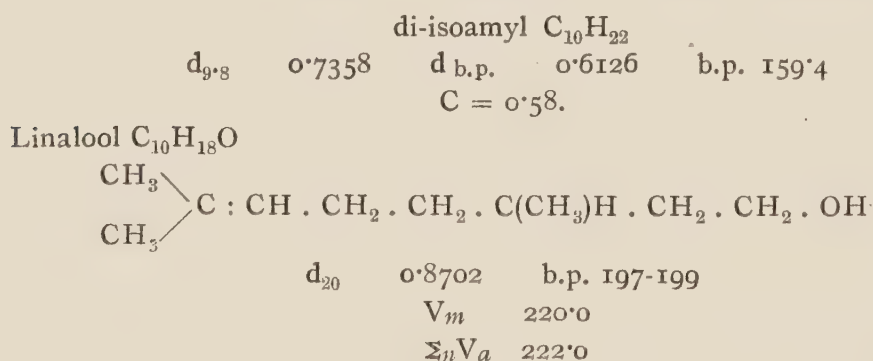


The minus value is due to the close approximation of the two groups. This is a maximum for the ortho compound.

### Terpenic Alcohols.

We may now, by means of the formula, investigate a number of alcohols, which are terpene derivatives, beginning with the olefin terpenes.

All the compounds are of complexity  $C_{10}$ , and thus we may use the data for di-isoamyl  $C_{10}H_{22}$  to calculate the value of  $C$ .



This result is remarkable considering the large differences which were found for the olefinic terpenes themselves.

The olefin terpene alcohols are seen to be open-chain hydrocarbons.

Moreover it has been shown that the group  $(CH_3)_2 C : CH -$  is responsible for a contraction of - 2.4, which would diminish



the value of  $\Sigma_n V_a$ , and so results in one very nearly equal to that shown by  $V_m$ .

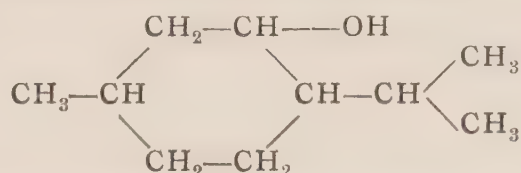
It is to be supposed that compounds like menthol  $C_{10}H_{20}O$  should agree with the characteristics of the class to which it belongs.

Thujamenthol, $d_{20}$	0.9015	b.p. 212	0.7389	$C = 0.554$ (thymol)
	$V_m = 211.1$			

From thymol we find—

Cymene $C_{10}H_{14}O'$	184.5 5.6
	190.1
less for ortho struct.	- 2.0
	188.1
6H	23.8
$\Sigma_n V_a = 211.9$	
$V_m = 211.1$ by form.	

There is thus agreement with the formula—



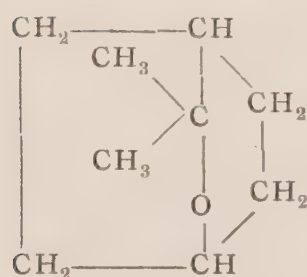
This compound possesses a contraction of  $-15.0$  for ring structure, and a contraction of  $-2.0$  for ortho structure, as for thymol.

Dihydrocarveol $C_{10}H_{18}O$				
$d_{20}$	0.927	b.p. 225°	$C = 0.550$	
			$d_{225}$	0.741
			$V_m$	207.8
			$\Sigma_n V_a$	222.0
			$\Delta$	- 14.2 for ring.

This at once enables us to place dihydrocarveol and similar compounds in their particular class—the menthan terpene alcohols.

A very interesting compound is—

Cineol  $C_{10}H_{18}O$ .

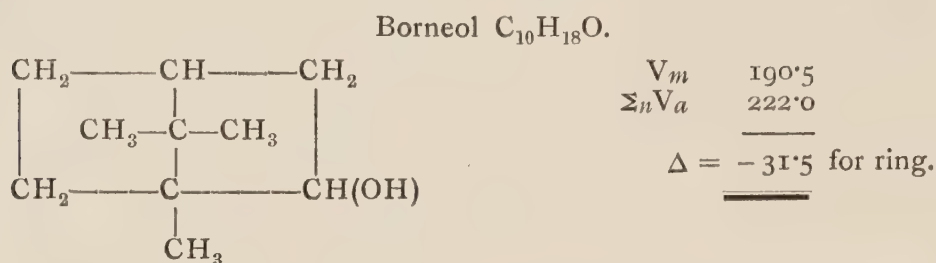


This substance has the following formula ascribed to it:—

$C = 0.46$ as is usual for ring compounds.			
b.p. 176	$d_{16}$	0.923	$d_{176}$ 0.792
$V_m$	194.0		
$\Sigma_n V_a$	222.0		
$\Delta = -28.0$ (for ring).			

Cineol thus belongs to the bridged ring class.

A compound of a similar character which has been specially studied is



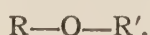
The value of  $\Delta$  for these compounds is about twice that for a single six-membered ring.

It seems probable that minor overlapping effects may disturb the result somewhat.

Thus  $2 \times -15.0 = -30.0$  for ring structure,  
and  $-1.5$  for ortho position of  $\text{CH}_3$  and  $\text{OH}$ .

In accord with this, we find that camphor, a CO compound, possesses a contraction of  $-30.0$  only.

### The Ethers.



Corresponding to the alkyl halogen compounds (halogen monovalent)



we find the ethers (  $\text{>O}$  divalent)



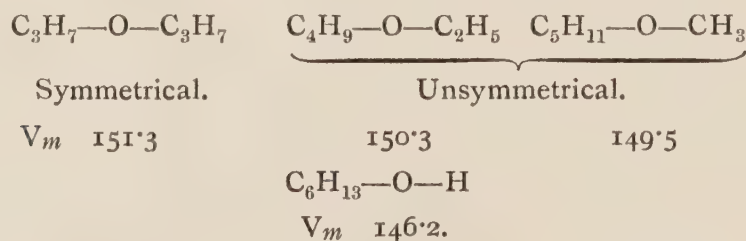
which involve the combination



These give results which are different to those characteristic of the combination which has just been studied, viz. :—



The following isomers of empirical formula  $C_6H_{14}O$  exist—



In the above compounds, there is a progressive change in volume from the symmetrical to the unsymmetrical types, and it

becomes smaller as the oxygen atom approaches the end of the chain.

An analogous variation is found in the case of the boiling-points, but in the opposite direction.

	(1)	(2)	(3)	(4)
b.p.	90.7	91.4	—	157.0

The last step of the change in boiling-point, that is, from the methyl ethers to the isomeric alcohols, is usually very great—about 70° C.

This corresponds to a volume change of 5 units. The following comparisons give the volumes of ethereal oxygen. The values of this atom are found by subtracting the volumes of the paraffins from those of the corresponding ethers.

TABLE LII.

<i>The Methyl Ethers.</i>			<i>The Symmetrical Ethers.</i>			<i>The Paraffins.</i>	
Compound.	V <sub>m</sub> .	>O.	Compound.	V <sub>m</sub> .	>O.	C <sub>n</sub> H <sub>2n+2</sub> .	V <sub>m</sub> .
C <sub>2</sub> H <sub>5</sub> —O—CH <sub>3</sub>	84.2	10.2	H—O—H CH <sub>3</sub> —O—CH <sub>3</sub>	18.9 62.7	11.5 10.7	H <sub>2</sub> C <sub>2</sub> H <sub>6</sub> C <sub>3</sub> H <sub>8</sub> C <sub>4</sub> H <sub>10</sub>	[7.4] [52.0] [74.0] 96.0
C <sub>3</sub> H <sub>7</sub> —O—CH <sub>3</sub>	105.9	9.9	C <sub>2</sub> H <sub>5</sub> —O—C <sub>2</sub> H <sub>5</sub>	106.4	10.4	C <sub>5</sub> H <sub>12</sub> C <sub>6</sub> H <sub>14</sub> C <sub>7</sub> H <sub>16</sub> C <sub>8</sub> H <sub>18</sub>	117.8 139.9 162.6 186.2
C <sub>4</sub> H <sub>9</sub> —O—CH <sub>3</sub>	127.5	9.7	C <sub>3</sub> H <sub>7</sub> —O—C <sub>3</sub> H <sub>7</sub>	151.3	11.4		
C <sub>5</sub> H <sub>11</sub> —O—CH <sub>3</sub>	149.5	9.6	C <sub>4</sub> H <sub>9</sub> —O—C <sub>4</sub> H <sub>9</sub>	197.8	11.5		

The mean value of >O in the methyl ether series, is 9.9, and in the symmetrical series 11.0. Also, there are similar variations in the two series, viz. first a decrease, and subsequently a gradual increase. These changes are, however, comparatively small.

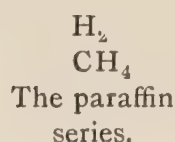
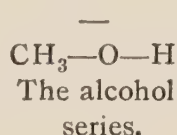
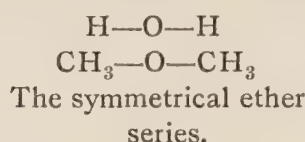
### The Position and Nature of Liquid Water.

It is very remarkable that, in accord with its simple formula, water should stand at the head of the symmetrical ether series—and is, in fact, its vanishing point.

In this it is analogous to hydrogen (H<sub>2</sub>) which is the vanishing point of the hydrocarbon series. In contrast to unsymmetri-



cal methyl alcohol, water is a symmetrical compound, and there is a corresponding difference in the volumes of O in the two compounds.



The formula apparently indicates the existence of a hydroxyl group, but it is more in accord with the formulæ for the symmetrical ethers.

As regards its volume, which is 18·7, we may suppose that it is made up as follows:—

$$[\text{H}_2\text{O}] = 2[\text{H}] + [\text{O}] = 2 \times 3\cdot7 + 11\cdot3 = 18\cdot7.$$

The volume of oxygen  $\text{>O}$  is thus 11·3.

This is considerably larger than that of hydroxyl oxygen as found in the alcohols.

$$[\text{C}_6\text{H}_{13}\text{OH}] = [\text{C}_6\text{H}_{14}] + [\text{O}] = 139\cdot9 + 6\cdot5 = 146\cdot4.$$

The volume of O' is thus 6·5, a number which is quite different from its former value. The volume of oxygen in water, however, agrees with the idea that on the whole it is ethereal in character. An examination of dimethyl ether shows this.

$$[(\text{CH}_3)_2\text{O}] = 2[\text{CH}_3\text{—}] + [\text{>O}] = 52\cdot0 + 10\cdot7 = 62\cdot7.$$

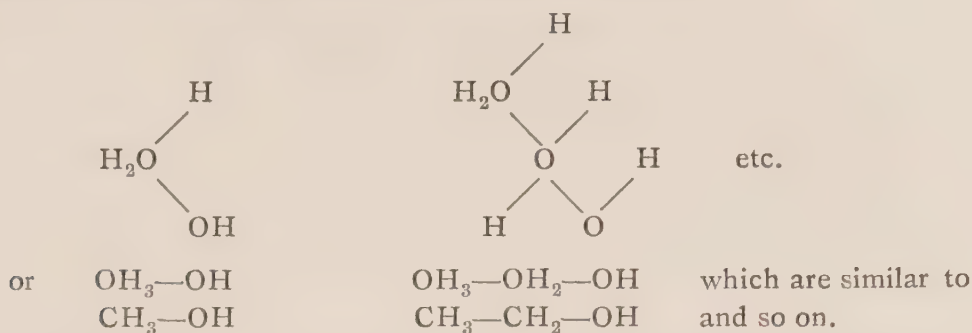
This value 10·7 is not very different from that obtained from an examination of water.

These calculations show that water is not a hydroxyl compound, but one of the symmetrical ethers.

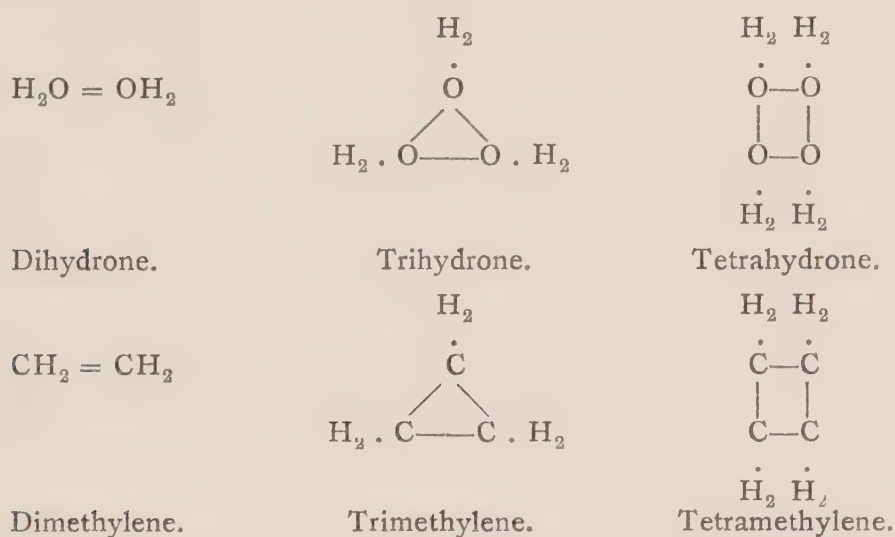
It has been known for some time that the simple formula  $\text{H}_2\text{O}$ , whilst doubtless representing one particular type of molecule, does not express the nature of water as a whole. Liquid water is an associated substance, that is, it is made up of molecules which are polymers of  $\text{H}_2\text{O}$ . Its formula might be expressed by  $(\text{H}_2\text{O})_x$ , where  $x$  is a number which is greater than unity. It is, moreover, known that the value of  $x$  cannot be expressed by a simple number, but water is a complex of many types of molecule.

Armstrong<sup>39</sup> has endeavoured to show that these fall into two classes.

(a) Those which are similar in configuration to the *paraffin or open-chain series*—in fact to the normal alcohols.



(b) *The hydrones* which are similar to ethylene and the *polymethylenes*.



These formulæ are consequent upon the assumption of quadrivalent functions by oxygen.

It may be shown, by means of molecular volumes, how far this hypothesis is justified at the boiling-point.

We do not know the volume of quadrivalent oxygen except as indicated by the single compound hydrogen-dioxide  $\text{H} - \text{O} \equiv \text{O} - \text{H}$ .

The volume of  $-\text{O} \equiv$  is found to be 8.0.

Since, with the exception of water, all of the above formulæ involve quadrivalent oxygen, the average volume cannot be greater than 15.4, if we consider compounds of class (a) alone and of complexity higher than  $(\text{H}_2\text{O})_2$ .

On the other hand, if we consider the influence of the hydrones, we come to the conclusion that the average volume would be considerably less if these existed in any large proportion, because ring compounds are subject to considerable contractions.

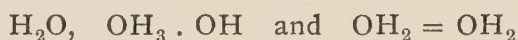
We are thus left with the simple molecule  $\text{H}_2\text{O}$  and the more complex ones,  $\text{OH}_2 = \text{OH}_2$  and  $\text{OH}_3 - \text{OH}$ .

The volume of  $\text{OH}_2 = \text{OH}_2$  would be 35.5, comparing it with ethylene. This gives an average value of 17.7.

The volume of  $\text{OH}_3 \cdot \text{OH}$  would be 36.2, or an average of 18.1 for  $\text{H}_2\text{O}$ .

If, however, we remember that the tendency of H is to increase the volumes of the simple compounds in which it occurs, as for example in  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{HCl}$  and the initial members of most series, the volume of simple  $\text{H}_2\text{O}$  at the boiling-point might be 20.0 or even more.

On the whole, we think that at the boiling-point liquid water might consist mainly of

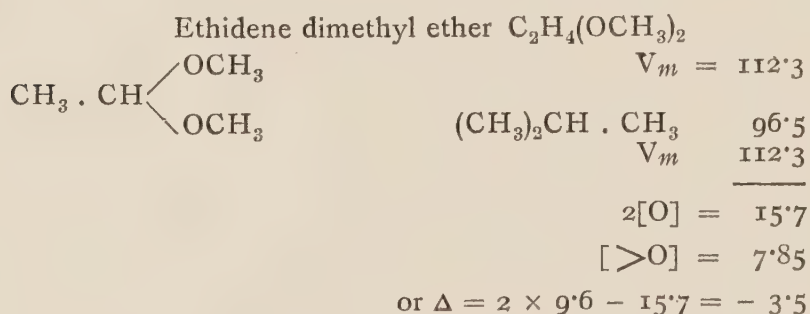


with perhaps smaller proportions of compounds of complexity  $(\text{H}_2\text{O})_3$ . It is not, however, probable that the other more complex compounds could occur, especially those which involve ring structure.

In accord with this we find that most physical properties show an association factor of between 2 and 3.

Physical Property.	Association Factor.
Capillarity (Ramsay and Shields) . . . . .	2.6
Mol. Cohesion (Walden) . . . . .	1.98
Volume (Traube) . . . . .	3.0
Fluidity (Bingham) . . . . .	2.2
Mean . . . . .	<u>2.4</u>

Certain other ethereal compounds are interesting.



This volume of the above ethereal oxygen is similar to what we find in  $\text{C}_6\text{H}_5\text{—O—CH}_3$ , but considerably less than in  $\text{C}_2\text{H}_5\text{—O—CH}_3$ .



Ethidene diethyl ether $C_2H_4(OC_2H_5)_2$		$V_m = 160.2$
$CH_3 \cdot CH \begin{cases} OC_2H_5 \\ OC_2H_5 \end{cases}$	$(C_2H_5)_2CH \cdot CH_3$	139.0
	$C_2H_4 \cdot (OC_2H_5)_2$	160.2
	$2 >O$	<u>21.2</u>
	$>O$	<u>10.6</u>

The volume of the ethereal oxygen is similar to what we find in  $C_6H_5-O-C_2H_5$ , and is more in accord with the number found in ethers of the type  $R-O-R'$ .

The above compounds thus show agreement with the ethers of the monohydric alcohols, in that the methyl group causes a depression in volume as compared with the volume when the ethyl group is present.

The explanation of the particular value found is not quite easy. The molecules are of the branched chain type of structure, the effect of which in this class of compound has not been studied sufficiently. In compounds with a single  $-OCH_3$  group, the depression is  $(10.6 - 9.6) 1.0$ , as compared with compounds with those having a single  $-OC_2H_5$  group.

In those with two  $-OCH_3$  groups, the total depression is  $2(10.6 - 7.85) = 2 \times 2.75$ . On the whole, there is an outstanding difference of 3.50.

### The Effect of the Addition of the Homologous Increment $CH_2$ on the Volumes of the Ethers.

The aliphatic ethers (see Dobriner, ref. 17) may be divided into series, e.g. that of the methyl ethers  $CH_3-O-CH_3$ , the ethyl ethers  $C_2H_5-O-C_2H_5$ , etc., each of which symmetrical compounds stands at the head of a series. The methyl  $CH_3$ , ethyl  $C_2H_5$ , etc., groups will appear on one side throughout the series, a radicle of variable complexity appearing on the other side.

It has been shown that the volumes of the ethers and those of certain esters are nearly the same, and that both series may be represented by a similar number of hydrogen equivalents  $W$ .

The ethers  $C_nH_{2n+2}O$  show values of  $W$  which are equal to  $6n + 5$ , because  $[>O] = [3H]$  and  $[C] = 4[H]$ .

The esters  $C_nH_{2n}O$  also show values of  $W$  equal to  $6n + 5$ , because  $O' = 2H$  and  $O'' = 3H$ .

If we know the molecular volume of a compound and the

number of hydrogen equivalents, the ratio  $V/W$  gives the volume of a single hydrogen equivalent. This enables us to find the variation in the volumes of H, and thus of every atom, throughout the homologous series.

TABLE LIII.—THE ALIPHATIC ETHERS.



The Dimethyl series.				The Diethyl series.			
W.	Compound.	$V_m$ .	$V/W$ .	W.	Compound.	$V_m$ .	$V/W$ .
17	$CH_3-O-CH_3$	62.6	3.680	29	$C_2H_5-O-C_2H_5$	106.2	3.664
23	$CH_3-O-C_2H_5$	84.2	3.660	35	$C_2H_5-O-C_3H_7$	128.1	3.659
29	$CH_3-O-C_3H_7$	105.1	3.624	41	$C_2H_5-O-C_4H_9$	150.3	3.666
35	$CH_3-O-C_4H_9$	127.5	3.643	—	—	—	—
—	—	—	—	—	—	—	—
53	$CH_3-O-C_7H_{15}$	195.0	3.680	59	$C_2H_5-O-C_7H_{15}$	221.3	3.751
59	$CH_3-O-C_8H_{17}$	220.2	3.732	63	$C_2H_5-O-C_8H_{17}$	247.2	3.803
Dipropyl series.				Dibutyl series.			
W.	Compound.	M.V.	$V/W$ .	W.	Compound.	M.V.	$V/W$ .
41	$C_3H_7-O-C_3H_7$	151.3	3.689	53	$C_4H_9-O-C_4H_9$	197.7	3.728
47	$C_3H_7-O-C_4H_9$	173.2	3.686	—	—	—	—
—	—	—	—	—	—	—	—
65	$C_3H_7-O-C_7H_{15}$	246.1	3.786	71	$C_4H_9-O-C_7H_{15}$	272.0	3.831
71	$C_3H_7-O-C_8H_{17}$	273.0	3.845	77	$C_4H_9-O-C_8H_{17}$	297.4	3.862

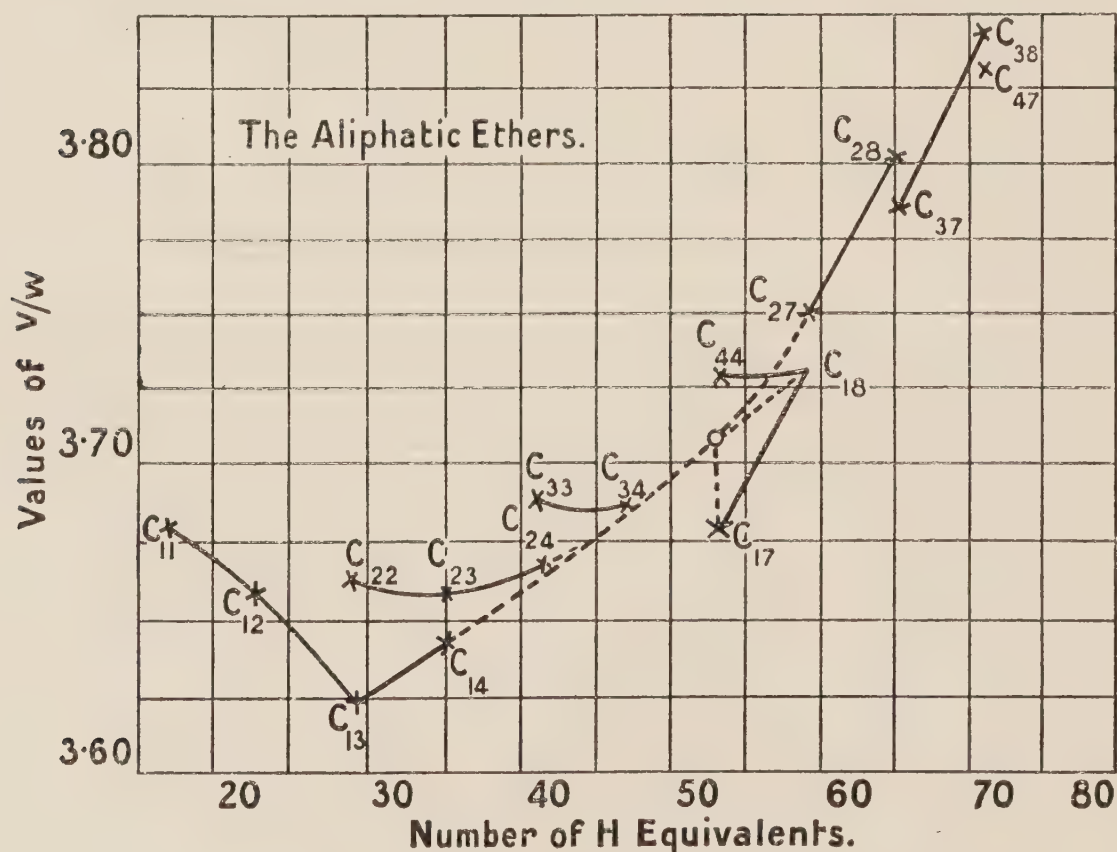


FIG. 3.

The above calculations show that, except at the beginning of series, there is a general increase in the value of  $V/W$ . Normally it should eventually be about 0.30 for each addition of  $\text{CH}_2$ . There are signs that this is the case, if we depend on the evidence of those series which do not include  $\text{C}_7\text{H}_{15}$  or  $\text{C}_8\text{H}_{17}$ .

The differences in the latter cases are over 0.50, which is double to that ordinarily found. This makes the slope of the curves for these complex compounds steeper than usual, e.g. as shown by the line  $\text{C}_{38}\text{C}_{37}$ , etc., in the diagram.

There is thus an apparent absence of continuity in the values of  $V/W$  between the simple and the more complex compounds. An examination of the  $\text{C}_5\text{H}_{11}$  and  $\text{C}_6\text{H}_{13}$  ethers would show whether this is real or not, and in the latter case, how the two are connected. An attempt has been made to show this connection in the curve for the ethyl ethers  $\text{C}_{22} \dots \text{C}_{28}$ . Excluding the methyl ether curve, which is different from the others, the curve just mentioned probably resembles in form those for other series as e.g. the normal paraffin series.

Thus, we find a nearly horizontal portion like  $\text{C}_{22}\text{C}_{23}\text{C}_{24}$  which includes a minimum. This minimum is very pronounced in the methyl ether curve, is still apparent in the next succeeding, and then practically disappears in the others.

Subsequently, we find an ascending portion which apparently is partly coincident with the ascending portion of the methyl ether curve  $\text{C}_{14} \dots \text{C}_{18}$ . This finally leaves the straight line, and the slope becomes steeper, as shown by the parts  $\text{C}_{27}\text{C}_{28}$ ,  $\text{C}_{37}\text{C}_{38}$ .

A remarkable fact, however, is, that the compound  $\text{C}_{17}$ , instead of finding its position on the line at a point marked  $\odot$ , is situated considerably below this, viz.  $V/W \ 3.708 - 3.680 = 0.28$ . If, however, we join the points  $\text{C}_{17}$  and  $\text{C}_{18}$ , we get a line which is parallel with the steeper portions of the heptyl and octyl curves, although  $\text{C}_{17}$  is out of position. This is all the more remarkable.

It follows from the fact that the gradients of  $\text{C}_{27}\text{C}_{28}$ , and  $\text{C}_{37}\text{C}_{38}$  are much steeper than has been found usual, and also that  $\text{C}_{17}\text{C}_{18}$  has a similar gradient, although  $\text{C}_{17}$  is out of position, that the molecular volumes of these and perhaps other compounds, are liable to vary from the expected values, from causes at present



unknown. These variations, however, do not seem to be due to experimental errors, nor to the existence of small quantities of accidental impurities. The whole question of the causes of the divergences of molecular volumes from those expected, and the causes of variation in the values given by various observers, is a difficult question, but well worth study. It is probable that unlooked for features might be discovered, either as applying to the molecules themselves, or to the characteristics of liquids.

### The Symmetrical and Unsymmetrical Ethers.

Ignoring the divergent values, and depending on the principle of continuity, we obtain the following curves shown in the diagram (Fig. 4).

I. *The curve for the symmetrical compounds.*

II. *The curve for the unsymmetrical compounds.*

III. *The curve for the methyl series.*

I. and II. are similar in *form*, which would lead us to conclude that the form is dependent on *complexity*, or the number of C atoms in the chain, and not on their character, symmetrical or otherwise.

Their *position* is, however, dependent on the *relative number* of C atoms on each side of the typical oxygen atom  $\text{>O}$  i.e. on the *degree of symmetry*.

Curve I. represents compounds of type  $\Delta n = 0$ , or the perfectly symmetrical.

Curve II. represents compounds of type  $\Delta n = 1$ , or compounds less symmetrical by one C atom.

This difference of one C in the radicles on either side of O is shown by a displacement of the curve in, say, the direction of increasing complexity, that is, there is a relative decrease in the value of  $V/W$  for want of symmetry.

In the case of the simpler compounds, an additional divergence from perfect symmetry is shown by an additional diminution in volume, but higher up this apparently vanishes, the compounds diverging more than  $\Delta n = 1$  from perfect symmetry, are nearly, if not entirely, of the same volume as those for which  $\Delta n = 1$  is true.

It is to be observed that the most symmetrical compounds, that is, those which stand at the head of each series, possess considerably larger volumes than those which might be expected. This gives that peculiar feature to the curves which may be observed from an inspection of the diagram, namely, that portion which occurs before the minimum, and which is marked by decreasing values of  $V/W$ . Since this characteristic also applies to the paraffin series, and as a matter of fact to all series, we see the analogy of these more symmetrical compounds with the first members of the other series. *Dimethyl oxide* is, for instance, a symmetrical compound, but it is also the first member of the *methyl ether* series, and corresponds to methane, methyl alcohol, methyl bromide. It seems to follow that the particular feature of symmetry, which is a characteristic of dimethyl ether, is that which also distinguishes the initial members of the other series, and which influences their volumes. Whether the cause be simple or complex, as indeed is probable, the operating influence is no doubt the general shape of the molecule and possibly its complexity or length of chain. For the present, limiting our view to the ether series, we distinguish two classes of compounds—

- (a) *the symmetrical* ;  
and (b) *the less symmetrical*,

that is, we have to distinguish those in which  $R - R' = O$  from those in which  $R - R' = CH_2$ . The special feature applying to the latter is apparently confined to the ether series and is additional to that which may apply to the compounds  $R - R' = O$ , as distinguished from those marked by the characteristic  $R - R' = nCH_2$ , and which includes all the members of the series which are less symmetrical than the absolutely symmetrical compounds.

Certain well marked diminutions are noticed in the compounds which are most unsymmetrical, i.e. those which contain a single methyl group, and sometimes, but to a lesser extent, those containing an ethyl and even propyl group. Whether this diminution is due to non-symmetry simply, or to the special influence of the  $CH_3$ ,  $C_2H_5$ , etc., groups, is a very difficult question to answer, and indeed is that one which presses most.

TABLE LIV.—THE ALIPHATIC ETHERS.

R—O—R'.							
Symmetrical.				Unsymmetrical.			
R—R'=O.				R—R'=CH <sub>2</sub> .			
W.	Compound.	V <sub>m</sub> .	V/W.	W.	Compound.	V <sub>m</sub> .	V/W.
17	CH <sub>3</sub> —O—CH <sub>3</sub>	62·6	3·680	—	—	—	—
—	—	—	—	23	CH <sub>3</sub> —O—C <sub>4</sub> H <sub>5</sub>	84·2	3·660
29	C <sub>2</sub> H <sub>5</sub> —O—C <sub>2</sub> H <sub>5</sub>	106·2	3·664	—	—	—	—
—	—	—	—	35	C <sub>2</sub> H <sub>5</sub> —O—C <sub>3</sub> H <sub>7</sub>	128·1	3·659
41	C <sub>3</sub> H <sub>7</sub> —O—C <sub>3</sub> H <sub>7</sub>	151·3	3·689	—	—	—	—
—	—	—	—	47	C <sub>3</sub> H <sub>7</sub> —O—C <sub>4</sub> H <sub>9</sub>	173·2	3·686
53	C <sub>4</sub> H <sub>9</sub> —O—C <sub>4</sub> H <sub>9</sub>	197·6	3·728	—	—	—	—
—	—	—	—	59	C <sub>4</sub> H <sub>9</sub> —O—C <sub>5</sub> H <sub>11</sub>	—	—
65	C <sub>5</sub> H <sub>11</sub> —O—C <sub>5</sub> H <sub>11</sub>	—	—	—	—	—	—
—	—	—	—	71	C <sub>5</sub> H <sub>11</sub> —O—C <sub>6</sub> H <sub>13</sub>	—	—
77	C <sub>6</sub> H <sub>13</sub> —O—C <sub>6</sub> H <sub>13</sub>	—	—	—	—	—	—
—	—	—	—	83	C <sub>6</sub> H <sub>13</sub> —O—C <sub>7</sub> H <sub>15</sub>	—	—
89	C <sub>7</sub> H <sub>15</sub> —O—C <sub>7</sub> H <sub>15</sub>	353·42	3·971	—	—	—	—
—	—	—	—	95	C <sub>7</sub> H <sub>15</sub> —O—C <sub>8</sub> H <sub>17</sub>	377·6	3·975

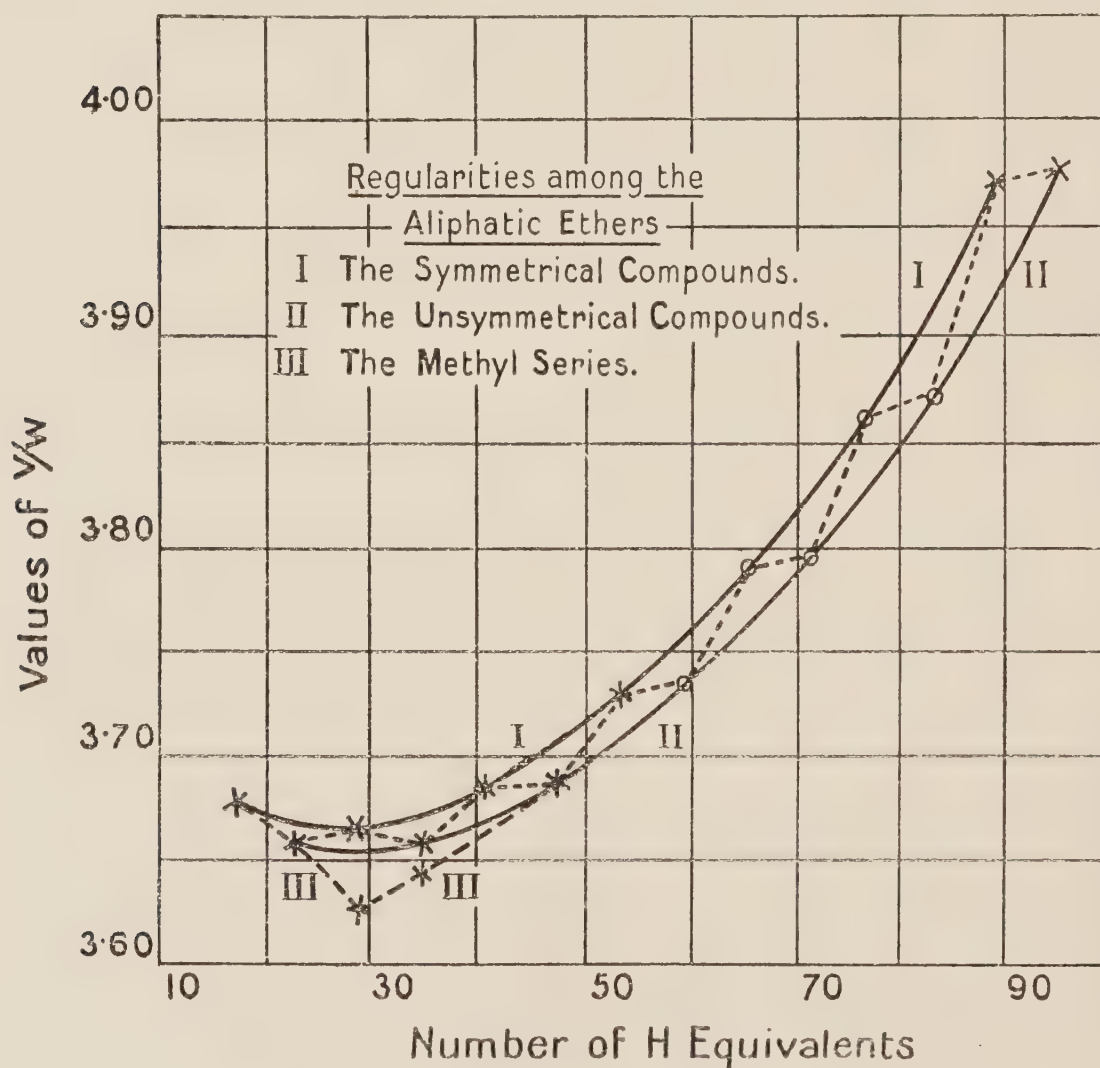


FIG. 4.



## Formula Representing the Results for Complexity and Symmetry in the Ethers. See Le Bas, Ref.<sup>40</sup>

An attempt has been made to represent the above results by a formula.

It has been shown that for the  $n$  paraffin and other series, the formula

$$V_m = W \{ S + (W - 40)K \}$$

reproduces the results—

W indicating the number of H equivalents ;

S the least or minimum volume of H in the series ;

K a number indicating the variation in volume of one H equivalent for an addition of one H or its equivalent.

The above-mentioned curves require a more complex formula to indicate them.

I. The *effect of complexity* is proportional to the *cube* of the number of C atoms.

$$\Delta_1 = \left( \frac{n}{2} - 2 \right) \left( \frac{n}{2} - 1 \right) \times 0.0101$$

and

II. The *effect of want of symmetry* is proportional to the *square* of the number of C atoms, the symbol  $n$  representing their number.

$$\Delta_2 = n_0 \times 0.003.$$

The *whole formula* is—

$$\text{M.V.} = (6n + 5) \left\{ 3.664 + \left( \frac{n}{2} - 2 \right) \left( \frac{n}{2} - 1 \right) \times 0.010 - n_0 \times 0.030 \right\}$$

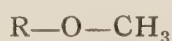
$$W = 6n + 5 \quad S = 3.664.$$

TABLE LV.—CALCULATION OF THE VOLUMES OF THE SYMMETRICAL AND UNSYMMETRICAL ETHERS BY MEANS OF FORMULA.

Class.	Compounds.	W.	$n$ .	V/W.	Corr. for unsymm.	V/W calc.	V/W obs.	V calc.	V obs.
S	CH <sub>3</sub> . O . CH <sub>3</sub>	17	2	3.664			3.677	62.25	62.5
U	CH <sub>3</sub> . O . C <sub>2</sub> H <sub>5</sub>	23	3	3.661	- 0.009	3.652	3.652	84.00	84.0
S	C <sub>2</sub> H <sub>5</sub> . O . C <sub>2</sub> H <sub>5</sub>	29	4	3.664		3.664	3.664	106.25	106.2
U	C <sub>2</sub> H <sub>5</sub> . O . C <sub>3</sub> H <sub>7</sub>	35	5	3.672	- 0.015	3.657	3.659	128.00	128.08
S	C <sub>3</sub> H <sub>7</sub> . O . C <sub>3</sub> H <sub>7</sub>	41	6	3.684		3.684	3.689	151.04	151.27
U	C <sub>3</sub> H <sub>7</sub> . O . C <sub>4</sub> H <sub>9</sub>	47	7	3.705	- 0.021	3.684	3.686	173.15	173.25
S	C <sub>4</sub> H <sub>9</sub> . O . C <sub>4</sub> H <sub>9</sub>	53	8	3.725		3.725	3.730	197.42	197.72
U	C <sub>4</sub> H <sub>9</sub> . O . C <sub>5</sub> H <sub>11</sub>	59	9	3.752	- 0.027	3.725	3.733	219.77	220.35
S	C <sub>5</sub> H <sub>11</sub> . O . C <sub>5</sub> H <sub>11</sub>	65	10	3.785		3.785	3.789	246.02	246.28
U	C <sub>5</sub> H <sub>11</sub> . O . C <sub>6</sub> H <sub>13</sub>	71	11	3.823	- 0.033	3.790	3.795	269.09	269.44
S	C <sub>6</sub> H <sub>13</sub> . O . C <sub>6</sub> H <sub>13</sub>	77	12	3.866		3.866	3.867	297.68	297.76
U	C <sub>7</sub> H <sub>15</sub> . O . C <sub>6</sub> H <sub>13</sub>	83	13	3.914	- 0.039	3.875	3.870	321.62	321.21
S	C <sub>7</sub> H <sub>15</sub> . O . C <sub>7</sub> H <sub>15</sub>	89	14	3.967		3.967	3.970	353.06	353.42
U	C <sub>8</sub> H <sub>17</sub> . O . C <sub>7</sub> H <sub>15</sub>	95	15	4.025		3.980	3.975	378.1	377.6

The compound (C<sub>8</sub>H<sub>7</sub>)<sub>2</sub>O is not given as its volume does not conform to the rule just given. Young<sup>41</sup> has, however, shown that the b.p. for this compound is too low. Given a higher number, there would probably be coincidence between the calculated and theoretical values.

In studying the compounds of the methyl series, either by means of Table LIII., or better from Fig. 3, we see the effect of a  $\text{CH}_3$  group on the volume of a compound



is, generally, to depress the volume. This is so at least down to the compound in which  $\text{R}=\text{C}_3\text{H}_7$ , but as R becomes less complex, the effect is an augmentation of  $\text{V}/\text{W}$ .

	$\text{V}/\text{W}$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_3$	3.624
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_3$	3.660
$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_3$	3.680

This result may be ascribed to a number of causes: (*a*) diminishing complexity, (*b*) increase of symmetry, (*c*) increase in the compactness of the molecule. Probably all of these influences contribute to the result, but they are not independent, and thus the analysis cannot be made.

### An Examination of the Various Constitutive Effects Associated with Hydrocarbon Chains.

In the following attempt to analyse the conditions which give to the molecular volumes of the ethers their particular character, it might seem that we look upon the factors as being independent one of the other. In reality, it is probable that they are *not independent*, so that real analysis is difficult, if not impossible. Still our view of things may not be without its advantages and of some interest.

The influences operating on hydrocarbon chains are:—

(*a*) *Complexity* with which may be included length of chain.

The effect of this is probably always to augment the atomic volume. By complexity we do not necessarily mean increase in the number of atoms, still less, and increase in the molecular weight, but rather increase in the number of units of volume (see Fig. 5).

This is, in normal chains, complicated by a second factor.

(*b*) One which is closely related to *compactness of molecular form*.

This is a maximum for the first member of each series—the methyl compound.

If we take the carbon atom as a centre, it is possible, by assuming that the shape of methane is a regular tetrahedron, to

describe a sphere about this centre so as to include all the H atoms. These H atoms would be situated on the surface of the sphere.

In the case of *ethane* and *propane*, etc., the corresponding figures would be gradually elongating ellipsoids of revolution.

Plane projection would show them as circles and ellipses.

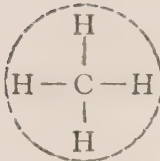
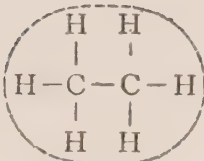
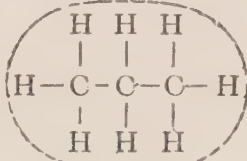
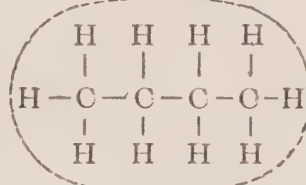
This compactness, or rather diminishing compactness, tends to diminish the atomic volume, but the observable influence of this factor, extends to only the fourth or fifth member of each series. At this point the influence of increasing complexity becomes predominant.

### The Influence of Compactness of Molecules.

Unbroken C Chains.

Homogeneous Attachments.

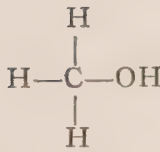
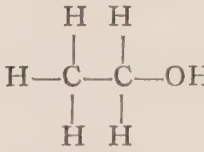
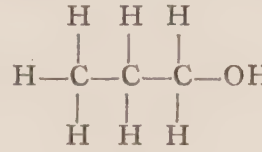
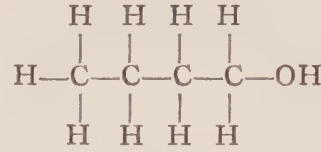
*The n Paraffin Series.*

			
V/W 4.85	4.05	3.72	3.693
No. of atoms in molecular chain. 1	2	3	4

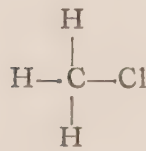
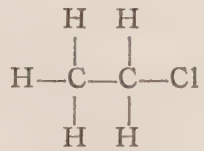
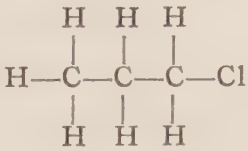
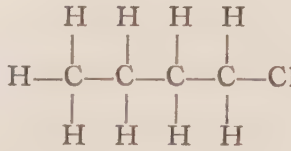
Unbroken Chains.

Heterogeneous Attachments.

*The Alcohol Series.* OH = 3 V/W.

			
V/W 4.28	3.88	3.70	3.647
No. of atoms in chain. 1	2	3	4

*The Chloride Series.* Cl = 6 V/W.

			
V/W 3.90?	3.774	3.668	3.661
No. of atoms in chain. 1	2	3	4



*The Bromide Series.* Br = 7.5 V/W.

	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Br} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{Br} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{Br} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{Br} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
V/W	3.84	3.780	3.672	3.649
No. of atoms in chain.	1	2	3	4

*The Iodide Series.* I = 10 V/W.

	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{I} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{I} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{I} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{I} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
V/W	3.770	3.730	3.683	3.663
No. of atoms in chain.	1	2	3	4

*Broken Carbon Chains.**The Ethers.*

	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
V/W	3.680	3.660	3.628
No. of atoms in chain.	3	4	5

	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$
V/W	3.664	3.659
No. of atoms in chain.	5	6

In the above-mentioned compounds the influence at work is, as it were, a *mutual repulsion* between the atoms attached to the same C atom.

Such a mutual repulsion is exerted by H, Cl, Br and I atoms among themselves, and the effect is a maximum when all the atoms attached to the carbon are of the same kind (see p. 125).

The rule, which may be applied to the different series, is, that *the volume tends to a maximum in a series, as the shape of the molecule becomes most compact, i.e. when it may be enveloped by a sphere of revolution.* This will naturally be the simplest member.

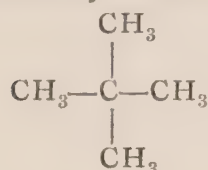
When there is reason to believe that mutual attractions are

possible, the above rule is no longer true. The effect indeed is exactly the opposite of the above. An example of this is found among the branched-chain hydrocarbons. The rule is:—

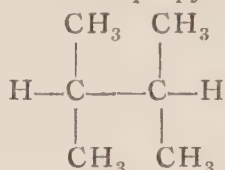
*That the volume tends to a minimum, as the shape of the molecule approximates to that of the sphere.*

An example of this attracting influence between groups is

Tetramethyl methane.



Di-isopropyl.



We should be inclined to attribute the expanding effect to the influence of the attached atoms H, Cl, Br, etc., but the contracting effect to a residual action of the intense self-affinity which characterizes carbon, and which persists in spite of the presence of the other atoms.

Closely associated with the above influence is a third—

(c) *The homogeneity or heterogeneity of the attached atoms.*

In studying the methyl and ethyl compounds belonging to the various series, we notice that when an atom or group other than hydrogen takes the place of hydrogen, the atomic volumes become smaller.

The amount of the diminution increases as the volume of the heterogeneous atom increases.

The diagram on next page better illustrates this.

The two curves—that for the methyl and ethyl compounds respectively, are very similar.

In both, we see that the volumes of the atoms diminish with an increase in volume of the heterogeneous atom attached to carbon.

*Homogeneity* then tends to *expand* the volumes, and *heterogeneity* to *contract* them.

This is well shown in the following—

	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \\   \\ \text{H}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$
V/W	4.85	3.88	3.617	3.674	3.704

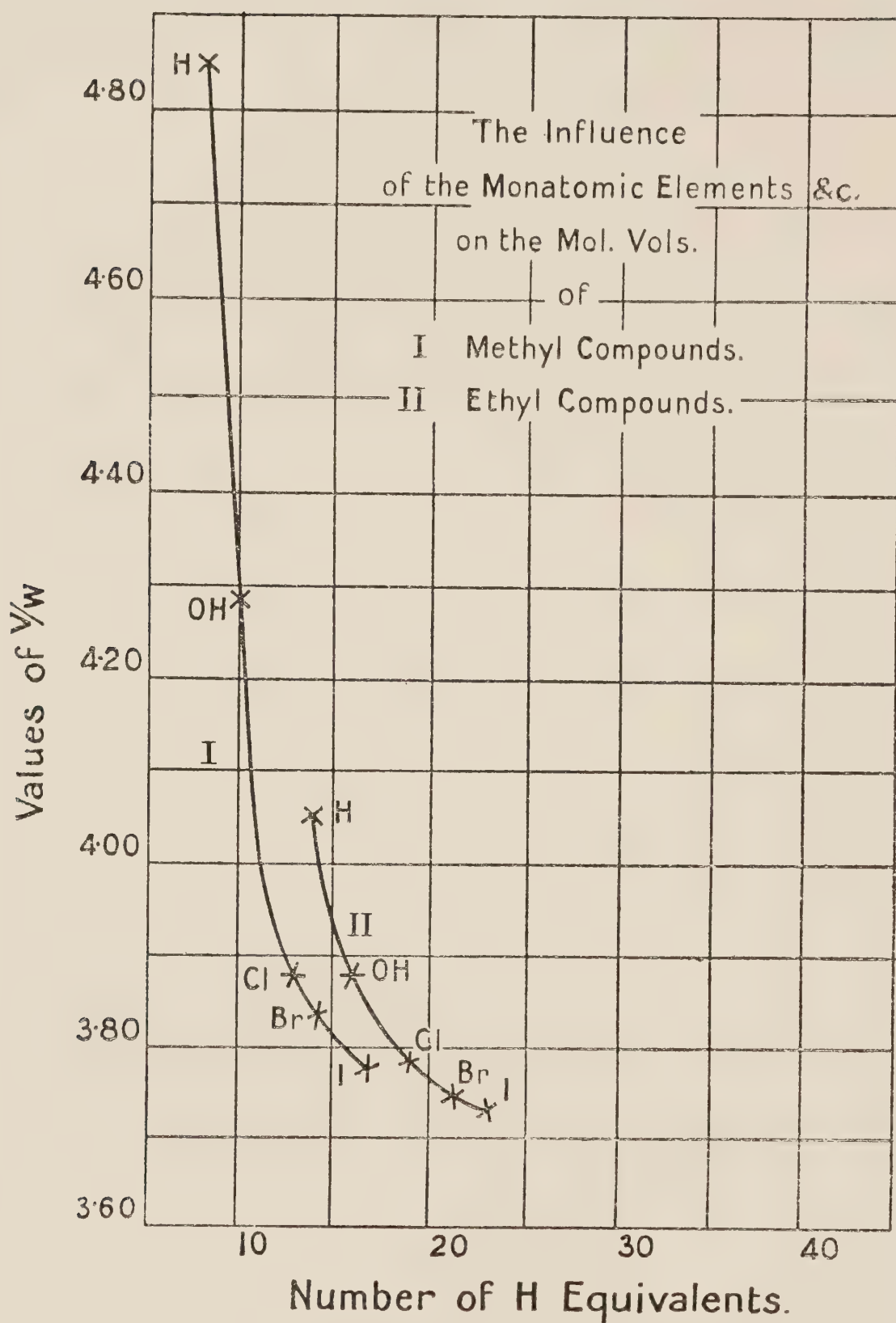


FIG. 5.



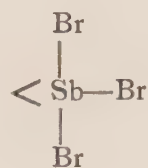
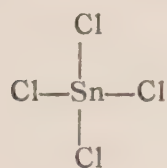
and also in the corresponding bromine compounds—

	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Br} \\   \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{Br} \\   \\ \text{Br} \end{array}$	$\begin{array}{c} \text{Br} \\   \\ \text{H}-\text{C}-\text{Br} \\   \\ \text{Br} \end{array}$	$\begin{array}{c} \text{Br} \\   \\ \text{Br}-\text{C}-\text{Br} \\   \\ \text{Br} \end{array}$
V/W	4·85	3·84	3·695	3·764	probably higher.

It will be noticed that there is an increase in complexity as well as a change in homogeneity as we proceed from left to right. *It is difficult to consider them apart.* The above values find their place on a curve similar in character to the curves for the normal series. The homologous increments in these cases are  $-\text{[H]} + \text{[Cl]}$  and  $-\text{[H]} + \text{[Br]}$ .

The effect due to homogeneity is much greater when the volatile hydrogen is present, than when replaced by the heavy chlorine atom.

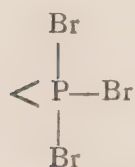
In compounds like



the halogen atoms possess their maximum values.

$$\text{Cl} = 22\cdot2 \quad \text{Br } 28\cdot0 \text{ or over.}$$

*Exception.*



In this case, the atomic volumes of Br are 27·0, similar in fact to that of P, instead of 28 or more.

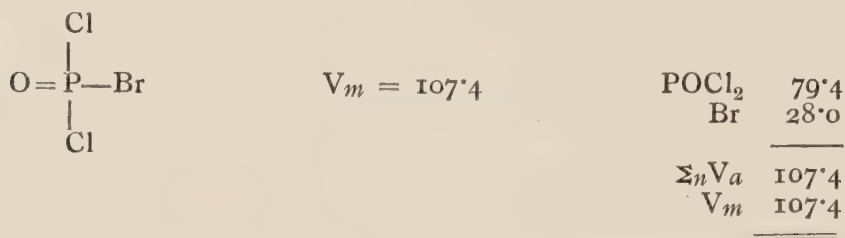
*Heterogeneity* on the other hand usually results in a diminution of the volume.

This has been shown to be the case in

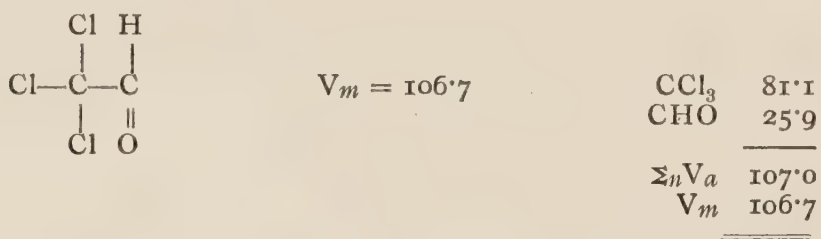
$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{CH}_2\text{Br}_2$		
$\begin{array}{c} \text{Cl} \\   \\ \text{Br}-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	$V_m \ 108\cdot4$	$\text{CCl}_3$	$81\cdot4$	$\text{Br } 27\cdot0$
$\begin{array}{c} \text{Cl} \\   \\ \text{NO}_2-\text{C}-\text{Cl} \\   \\ \text{Cl} \end{array}$	$V_m \ 110\cdot9$	$\text{CCl}_3$	$81\cdot4$	$\text{NO}_2 \ 29\cdot5$
				Normal $32\cdot0$

Thus the effect of homogeneity is an apparent repulsion between the atoms attached to the central atom, and the effect of heterogeneity is an attraction. These influences respectively produce expansions and contractions.

The following cases are also interesting :—



which corresponds to

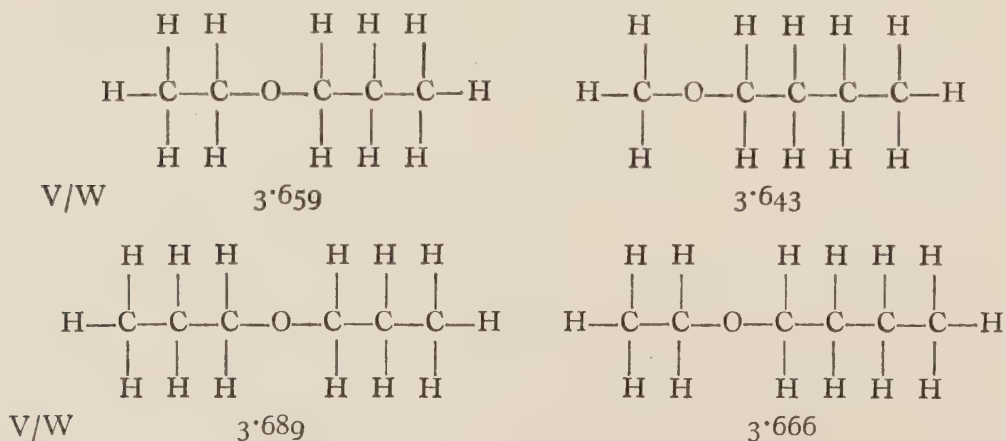


The atom : O does not seem to be able to act in a manner similar to that of the monatomic elements with single linkings or with groups like  $\text{NO}_2$  singly linked.

It should be remarked that whereas chlorine atoms attached to the *same* carbon atom give rise to *expansions*, or, perhaps, more accurately, allow the volumes of the atoms to attain their full value, on the contrary, when they are attached to *different* carbon atoms, they cause *contractions*. This is an additional feature which has already been noticed.

(d) *Symmetry*. The effect of this has also already been investigated, at any rate in the case of the ethers.

Thus in the compounds  $\text{C}_6\text{H}_{14}\text{O}$  and  $\text{C}_5\text{H}_{12}\text{O}$  we find the following characteristics.



In both of the above instances the complexity is the same, as also the degree of compactness of the molecule, but the degree of symmetry or distribution of carbon atoms about the oxygen atom is different.

The most symmetrical compound possesses the largest volume, and the values of  $V/W$  diminish as the degree of symmetry becomes less.

In the ethers at any rate, degree of complexity modifies the effect of symmetry, or rather want of it. Thus the effect of want of complete symmetry among the higher compounds is not nearly so marked as among compounds lower down in the series.

The effect of degree of symmetry on the volumes of the atoms, and thus on the molecular volumes, is best shown by some of the esters of the monocarboxylic acids.

TABLE LVI.—ISOMERIC ESTERS.

$C_7H_{14}O_2$	M.V.	B.P.	$C_8H_{16}O_2$	M.V.	B.P.
$C_5H_{11} \cdot CO \cdot O \cdot CH_3$	172.2	149.6	$C_6H_{13} \cdot CO \cdot O \cdot CH_3$	196.2	173.0
$C_4H_9 \cdot CO \cdot O \cdot C_2H_5$		144.6	$C_5H_{11} \cdot CO \cdot O \cdot C_2H_5$	197.7	167.0
$C_3H_7 \cdot CO \cdot O \cdot C_3H_7$	174.0	143.0	$C_4H_9 \cdot CO \cdot O \cdot C_3H_7$	197.8	167.0
$C_2H_5 \cdot CO \cdot O \cdot C_4H_9$		146.0	$C_3H_7 \cdot CO \cdot O \cdot C_4H_9$	197.8	165.7
$CH_3 \cdot CO \cdot O \cdot C_5H_{11}$		148.0	$C_2H_5 \cdot CO \cdot O \cdot C_5H_{11}$		
$H \cdot CO \cdot O \cdot C_6H_{13}$	173.3	153.2	$CH_3 \cdot CO \cdot O \cdot C_6H_{13}$	197.7	169.0
			$H \cdot CO \cdot O \cdot C_7H_{15}$	196.7	176.0

We see that the *most symmetrical* compound possesses the largest volume and the lowest boiling-point, whilst, on the other hand, the *least symmetrical* compound possesses the smallest volume and the highest boiling-point.

In the above series, as distinct from that of the ethers, the least symmetrical compounds are at the beginning and ends of the series, and the most symmetrical compounds are situated near the *middle*.

In *molecular volumes* there is thus a rule analogous to that stated by Hinrichs,<sup>42</sup> 1868, for the boiling-point, which is, *that the more symmetrical the formula of an isomeric molecule is the lower is the boiling-point*. This is similar to Naumann's statement of it (1874). The effect on volume is of the nature of an expansion.

### The Phenolic and Other Ethers.

The group  $—O—R$  can be attached to a radicle of the type  $C_6H_5—$  as well as to an aliphatic radicle  $R'$ .

$R'—O—R$   
Aliphatic ether.

$C_6H_5—O—R$   
Phenolic ether.



The phenols and similar compounds have already been studied, and it has been shown that there is a contraction of 0·8 as compared with the alcohols, when the methyl group is present.

TABLE LVII.—PHENOLIC ETHERS.<sup>43</sup>

		$V_m$ .		
Phenol methyl ether anisol	$C_6H_5 \cdot O \cdot CH_3$	125·5 }	O'	7·3
Toluene	$C_6H_5 \cdot CH_3$	118·2 }		
Phenetol	$C_6H_5 \cdot O \cdot C_2H_5$	149·3 }	O'	10·0
Ethyl benzene	$C_6H_5 \cdot C_2H_5$	139·3 }		
Phenyl propyl oxide	$C_6H_5 \cdot O \cdot C_3H_7$	172·4 }	O'	10·0
Propyl benzene	$C_6H_5 \cdot C_3H_7$	162·2 }		
Phenyl butyl oxide	$C_6H_5 \cdot O \cdot C_4H_9$	195·7 }	O'	11·2
Butyl benzene	$C_6H_5 \cdot C_4H_9$	184·5 }		

TABLE LVIII.—CRESYLIC ETHERS.

		$V_m$ .		
<i>p</i> Cresyl methyl oxide	$C_6H_4(CH_3) \cdot O \cdot CH_3$	147·6 }	O'	7·1
<i>p</i> Xylene	$C_6H_4(CH_3)_2$	140·5 }		
<i>p</i> Cresyl ethyl oxide	$C_6H_4(CH_3) \cdot O \cdot C_2H_5$	172·5 }	O'	10·2
<i>p</i> Ethyl toluene	$C_6H_4(CH_3) \cdot C_2H_5$	162·3 }		
<i>p</i> Cresyl propyl oxide	$C_6H_4(CH_3) \cdot O \cdot C_3H_7$	196·5 }	O'	11·6
<i>p</i> Propyl toluene	$C_6H_4(CH_3) \cdot C_3H_7$	184·9 }		

In comparing the aliphatic and aromatic ethers, in respect of the volume of O', we notice that it is only the methyl compounds which differ, 9·6 and 7·2 respectively. When the groups are more complex, there is very little difference between the volumes of O'.

#### *A Study of the More Complex Aromatic Ethers.*

The more complex ethers possess additional expansions owing to their increase in complexity.

Thus

Phenyl heptyl oxide	$C_6H_5-O-C_7H_{15}$	$V_m = 271·4$
	$C_6H_5$	92·8
	O''	10·0
	$C_7H_{15}$	158·9
	$\Sigma_n V_a$	261·7
	Observed	271·4

$$\Delta = + 9·7 \quad 3 \times 3·2 (C_7-C_4)$$

Phenyl octyl oxide	$C_6H_5-O-C_8H_{18}$	$V_m = 296·8$
	$C_6H_5$	92·8
	O''	10·0
	$C_8H_{17}$	181·0
	$\Sigma_n V_a$	283·8
	Observed	296·3

$$\Delta = + 12·5 \quad 4 \times 3·15 (C_8-C_4)$$

A slight increase is noticed at  $\text{—O—C}_4\text{H}_9$ , but after this there is an increase of 3.2 for every addition of  $\text{CH}_2$ .

### The Thymols.

Methyl thymol	$\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_3 \cdot (\text{CH}_3)\text{OCH}_3$	$V_m = 214.8^*$
	Cymene $\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$	184.7
	less H	3.2
		<hr/>
		181.5
	O'	7.4
	$\text{CH}_3$	25.5
		<hr/>
	$\Sigma_n V_a$	214.4
	$V_m$	214.8
		<hr/>

Ethyl thymol	$\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_3(\text{CH}_3)\text{OC}_2\text{H}_5$	$V_m = 240.5$
	Cymene $\text{C}_{10}\text{H}_{14}$ less H	181.5
	$\text{C}_2\text{H}_5$	48.0
	O'	11.0
		<hr/>
	$\Sigma_n V_a$	240.5
	$V_m$	240.5
		<hr/>

$\text{C}_6\text{H}_4$	89.6
O'	5.6
$\text{C}_3\text{H}_7$	70.0
$\text{CH}_3$	25.5
	<hr/>
$\Sigma_n V_a$	190.7
$V_m$	189.3
	<hr/>

$-1.4$  for O structure.

This is all the more remarkable seeing that the ortho cresylic ethers show it.

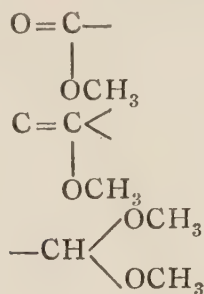
It follows from the above calculations that

$\text{—O—CH}_3$  gives a value of O' equal to 7.4  
 $\text{—O—C}_2\text{H}_5$  and  $\text{—O—R}$  } gives values of O' equal to 10-11.

When the total value of the side chains equals  $\text{C}_4$  or  $\text{C}_5$  there is a large increase in the volumes. This is due to complexity and involves every atom in the compound.

Since the volume of  $\text{—OCH}_3$  is the same in aliphatic methyl esters, and in aromatic methyl ethers, we are inclined to connect the contraction with the presence of unsaturation. Note the following:—

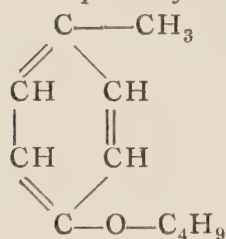
\* None of the thymol ethers show any contraction for ortho structure (*vide infra*). Compare thymol itself (q.v.)



in all of which  $\Delta\text{O} = 7-8$ , and compare with this  $\text{R}-\text{O}-\text{CH}_3$  in which  $\Delta\text{O} = 9.6$ . The conclusion before arrived at, seems the only one possible.

### The Cresylic Ethers.

*p* Cresyl butyl oxide



$\text{C}_6\text{H}_4(\text{CH}_3)\text{O} \cdot \text{C}_4\text{H}_9$

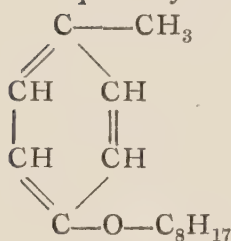
$V_m = 221.3$

$\text{C}_6\text{H}_4$	89.6
$\text{CH}_3$	25.5
$\text{O}'$	10.0
$\text{C}_4\text{H}_9$	92.3

$\Sigma_n V_a$	217.4
$V_m$	221.3

$$\Delta = + 3.9 \quad 1 \times 3.9 (\text{C}_5 - \text{C}_4)$$

*p* Cresyl octyl oxide



$\text{C}_6\text{H}_4(\text{CH}_3) \cdot \text{OC}_8\text{H}_{17}$

$V_m = 323.1$

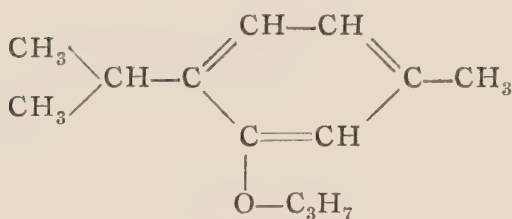
$\text{C}_6\text{H}_4$	89.6
$\text{CH}_3$	25.5
$\text{O}'$	10.0
$\text{C}_8\text{H}_{17}$	181.0

$\Sigma_n V_a$	306.1
$V_m$	323.1

$$\Delta = + 17.0 \quad 5 \times 3.4 (\text{C}_9 - \text{C}_4)$$

### The Thymols.

Propyl thymol



$\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_3(\text{CH}_3)\text{OC}_3\text{H}_7$

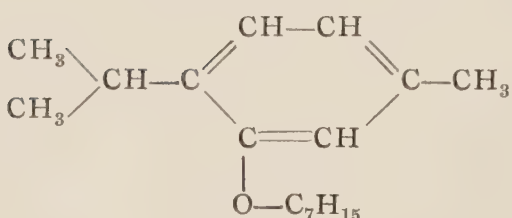
$V_m = 267.5$

$\text{C}_{10}\text{H}_{13}$	181.0
$\text{O}'$	10.0
$\text{C}_3\text{H}_7$	70.0

$\Sigma_n V_a$	261.0
$V_m$	267.5

$$\Delta = + 6.5 \quad 2 \times 3.2 (\text{C}_7 - \text{C}_5)$$

Heptyl thymol



$\text{C}_3\text{H}_7 \cdot \text{C}_6\text{H}_3(\text{CH}_3)\text{OC}_7\text{H}_{15}$

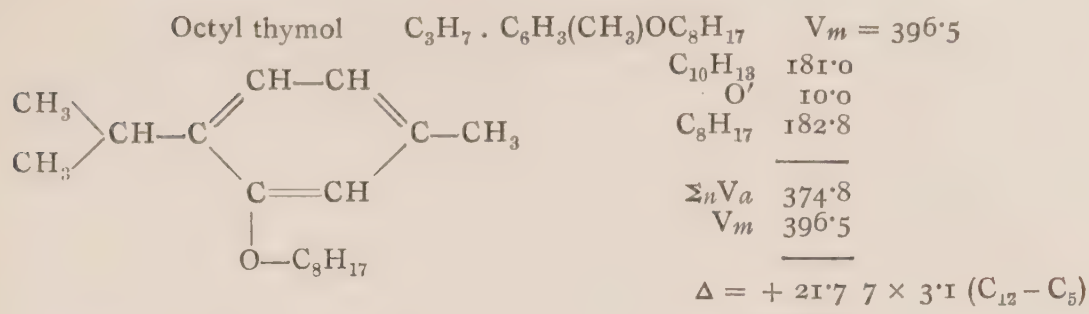
$V_m = 369.5$

$\text{C}_{10}\text{H}_{13}$	181.0
$\text{O}'$	10.0
$\text{C}_7\text{H}_{15}$	159.0

$\Sigma_n V_a$	350.0
$V_m$	369.5

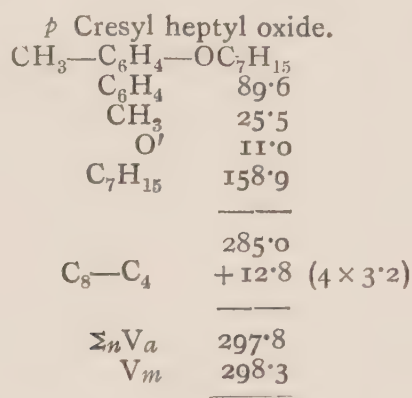
$$\Delta = + 19.5 \quad 6 \times 3.2 (\text{C}_{11} - \text{C}_5)$$





The increase in volume for complexity is seen to be apparently linear. This increase starts from approximately the same point in all the series, viz. where the *total* complexity of the side chains is  $C_4$ . Apparently it does not matter whether the chains are entire, or divided up, for this to occur. This indicates an increase in volume due to a corresponding increase in complexity as distinct from an increase in length of chain. The increase starts from  $C_5$  which is similar to what is observed in open chains. We conclude that the nucleus exerts no influence at all. Octyl thymol is interesting, as being the most complex compound which has been studied in this work. It consequently possesses the largest volume which is one of nearly 400 units.

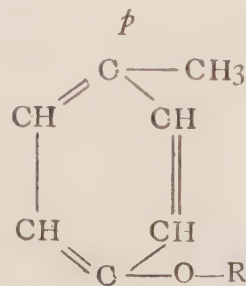
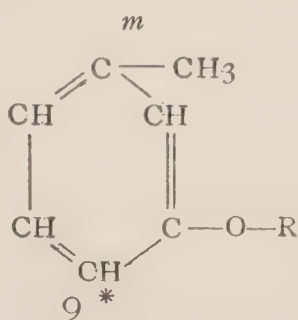
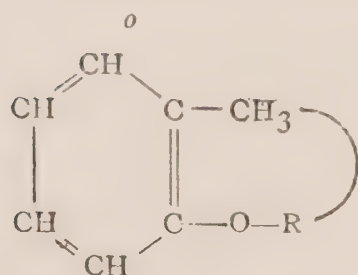
The calculation of the volume of an ether of the type mentioned is as follows:—



#### *The o, m, and p Cresylic Ethers.*

It has been shown that when two groups occupy the ortho-position, there are usually contractions.

$$C_6H_4 = 89.6 \quad CH_3 = 25.5 \quad C_2H_5 = 48 \quad O' = 7.4 \text{ or } 11.0 \quad C_n - C_4 = 3.2 (n-4).$$



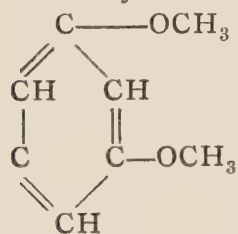
Groups $\text{CH}_3$ and $\text{OCH}_3$			$\Sigma_n V_a$
146.4	147.8	148.0	148.0
$\Delta$ -1.6	-0.2	$\pm 0$	
$\text{CH}_3, \text{OC}_2\text{H}_5$			
171.2	172.7	172.8	173.1
-1.6	-0.1	$\pm 0$	
$\text{CH}_3, \text{OC}_3\text{H}_7$			
195.4	196.7	196.5	195.1
-1.1	—	$\pm 0$	
$\text{CH}_3, \text{OC}_4\text{H}_9$			
218.8	221.0	221.3	221.4
-2.5	-0.3	$\pm 0$	
$\text{CH}_3, \text{OC}_7\text{H}_{15}$			
293.6	297.4	298.3	298.0
-4.7	-0.9	$\pm 0$	
$\text{CH}_3, \text{OC}_8\text{H}_{17}$			
318.6	322.7	323.1	323.4
-4.5	-0.4	$\pm 0$	

The magnitude of the contraction evidently increases as —OR becomes more complex, thus showing the existence of a special relation between the two groups.

There is thus a large contraction when the groups are in the ortho-position relative to each other. This appears to increase in magnitude as the complexity of R increases. The above contractions are regarded as being due to a mutual action of the group, owing to residual affinity.

The following compound is worthy of separate study:—

Dimethyl resorcin.



$V_m$	157.7
$\text{C}_6\text{H}_4$	89.6
20'	14.8
$2\text{CH}_3$	52.0
$\Sigma_n V_a$	156.4
$V_m$	157.7

The oxygen atoms are probably augmented in value, as compared with its value in previous compounds, owing to the fact that there are two—8.0 e.g. The value of  $\text{O}'$  in  $-\text{OCH}_3$  is, however, still considerably below that for  $\text{O} \cdot \text{C}_2\text{H}_5$  — 10 units. It will have been repeatedly observed that the methyl group always causes a diminution in volume as compared with the ethyl, etc.

**Oxygen with Double Linking.**

= O.

(Attached to carbon.)

The simplest compound is—

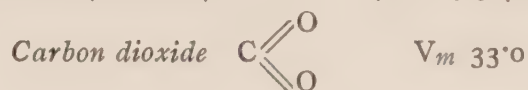


Carbon in this instance is divalent, and it has not been shown whether divalent carbon possesses the same volume as quadrivalent carbon or not. An examination of such groups as CHO and CO, *under certain circumstances*, shows that in combination,  $\text{CO} = 22\cdot1$ .

$\text{C}_3\text{H}_7 \cdot \text{CHO}$	96·0
$\text{C}_3\text{H}_8$	74·0
	<hr/>
CO	22·0
	<hr/>

It follows that the oxygen under these circumstances (i.e. when carbon is quadrivalent  $\text{C}^{\text{iv}}$ ) is the same as when it is divalent.

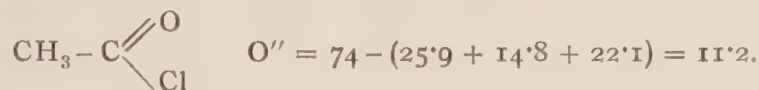
$$\text{O}'' = (\text{CO} - \text{C}) = 22\cdot1 - 14\cdot8 = 7\cdot3 \ (\text{H}_2)$$



$$\text{The volume of C} = 14\cdot8 \quad \therefore \text{O}_2 = 18\cdot7.$$

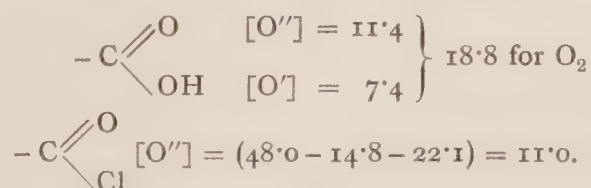
It is remarkable that the volume occupied by  $\text{O}_2$  is the same as the volume of  $\text{O}_2$  in the esters —  $\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O(R)} \end{array}$  and similar to the one calculated from the acids —  $\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O(H)} \end{array}$ .

Moreover if the volumes of certain compounds containing the group —  $\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{Cl} \end{array}$  are considered, these compounds being derivatives of the acids, we see that the volume of :O is 11·0.



$$\text{Moreover } [\text{O}''] = 33\cdot5 - 22\cdot1 = 11\cdot4.$$

It is possible that the two oxygen atoms may possess different volumes (a)  $[\text{O}'] = 7\cdot4(2\text{H})$ , (b)  $[\text{O}''] = 11\cdot0(3\text{H})$ .





An alternative supposition is that the volumes of oxygen (O'') are similar, i.e.  $[O''] = 18.8 \div 2 = 9.4$ .

### The Aldehydes and Ketones.

In dealing with compounds which contain doubly bound oxygen, we come to the conclusion that the position of this atom in the side chain has some influence on the volume. Comparing the ketones and the aldehydes we find:—

$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH} \\ \parallel \\ \text{O} \end{array}$ <p>Acetaldehyde <math>V_m = 74.8</math></p> $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \\ \parallel \\ \text{O} \end{array}$ <p>Propaldehyde <math>V_m = 96.0</math></p> $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \\ \parallel \\ \text{O} \end{array}$ <p>Butyraldehyde <math>V_m = 118.2</math></p>	$\begin{array}{c} \text{CH}_3 - \text{C} - \text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ <p>Acetone <math>V_m = 77.1</math></p> $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ <p>Methyl ethyl ketone <math>V_m = 96.7</math></p> $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ <p>Methyl propyl ketone <math>V_m = 118.5</math></p> $\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ <p>Diethyl ketone <math>V_m = 117.7</math></p>
---	---

These compounds are difficult to deal with.

(a) On the one hand, we have one factor involved, which is the position the compound occupies in its particular series.

We should expect the acetaldehyde and acetone to be relatively larger than the volumes calculated on the basis of  $C = 14.8$ ,  $H = 3.7$ , and thus be not quite comparable with the succeeding members of each series.

(b) There is also the question of the influence of symmetry. Both of these factors might be considered to be of influence on the volumes, and to explain the differences.

Observation, however, shows that there is something wanting in this kind of explanation.

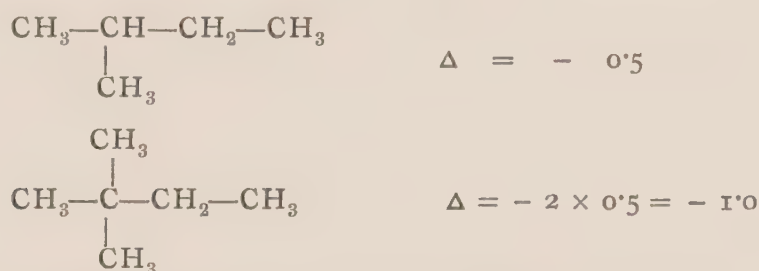
The study of molecular volumes has made the want of a comprehensive generalization, which would cover all these cases, very keenly felt. The good results which have attended the study of some series show that we are getting nearer to the discovery of such a generalization.

If we relinquish such purely geometrical ideas as symmetry, and introduce the more chemical notion of a specific influence of

certain atoms or groups, we seem to be getting nearer to the desired end. After all, the question of symmetry may be involved, but only in a subordinate sense. The particular arrangements of the atoms in a compound are bound to have some influence on the volume, and among them their symmetrical arrangement about the distinctive atom or group of the compound. It is possible for there to be a yet more fundamental explanation, which may lie in the direction of the alternative one already suggested.

It must especially be noted that the volume variations in the series of compounds including the aldehydes and ketones of various kinds seem inseparably connected with similar variations in the boiling-points. Compounds with :O at the end of the chain have the smallest volumes and boiling-points. The volumes apparently increase as :O becomes attached to intermediate carbon atoms.

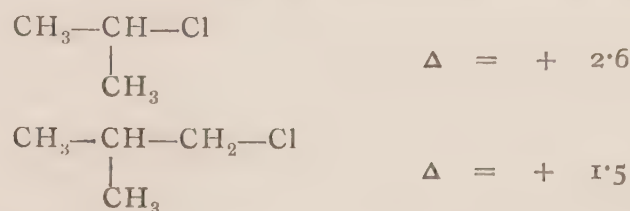
It has been shown that when the iso group is present in a pure hydrocarbon (paraffin, etc.), there is a contraction.



These contractions are connected with the presence of methyl groups which probably are not saturated. In such a modification as—



there is an increase in the contraction, owing to the presence of the ethenoid linkage, in close proximity to the iso group. In some paraffin derivatives we, however, get a different result :—



Whilst the association of two hydrocarbon radicles, or a hydrocarbon radicle and one which contains an ethenoid linkage,

occasions a contraction, the association of a hydrocarbon group and a halogen atom produces an expansion. It is evident that the methyl  $\text{CH}_3$  group exerts a more powerful influence than an ethyl group, and the extent of the influence of the halogen atoms is in the order indicated by chlorine, bromine, and iodine.

In studying the groups, we find that there is a depressing effect due to the simple radicle, which diminishes as this becomes larger. The effect is thus in the inverse order of—



We have now to consider the influence of  $\text{H, CH}_3, \text{C}_2\text{H}_5$ , etc., on  $\text{C}:\text{O}$ . As in the halogen compounds, the substitution of  $\text{:O}$  for  $\text{H}_2$  increases the volume. The atom hydrogen does not seem to have much effect, but that of the methyl group is considerable, whilst it is progressively smaller for  $\text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$ —

(1) $\text{CH}_3 \cdot \text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{O} \end{array}$	$V_m = 56.7 \quad \Sigma_n V_a \quad 51.9 \quad \Delta + 4.8 \quad (\text{CH}_3 \text{ and H})$
(2) $\text{C}_2\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{O} \end{array}$	$V_m = 74.8 \quad ,, \quad 74.0 \quad + 0.8 \quad (\text{C}_2\text{H}_5 \text{ and H})$
(3) $\text{CH}_3 \cdot \text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{O} \end{array}$	$V_m = 77.1 \quad ,, \quad 74.0 \quad + 3.1 \quad (\text{two CH}_3)$
(4) $\text{C}_3\text{H}_7 \cdot \text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{O} \end{array}$	$V_m = 96.0 \quad ,, \quad 96.0 \quad — \quad (\text{C}_3\text{H}_7 \text{ and H})$
(5) $\text{C}_2\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{O} \end{array}$	$V_m = 96.7 \quad ,, \quad 96.0 \quad \Delta + 0.7 \quad (\text{CH}_3 \text{ and C}_2\text{H}_5)$
(6) $\text{C}_4\text{H}_9 \cdot \text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{O} \end{array}$	$V_m = 118.2 \quad ,, \quad 118.2 \quad \Delta \quad — \quad (\text{C}_4\text{H}_9 \text{ and H})$
(7) $\text{C}_3\text{H}_7 \cdot \text{C} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{O} \end{array}$	$V_m = 118.5 \quad ,, \quad 118.2 \quad \Delta + 0.5 \quad (\text{C}_3\text{H}_7 \text{ and CH}_3)$
(8) $\text{C}_2\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{C}_2\text{H}_5 \\ \diagdown \text{O} \end{array}$	$V_m = 117.7 \quad ,, \quad 118.2 \quad \Delta - 0.5 \quad (\text{two C}_2\text{H}_5)$

It is seen that wherever we find one or two methyl groups we find a large positive effect. That due to the  $\text{C}_2\text{H}_5$  group is less.

Whilst the above seems clear, we must also consider another factor—the total complexity of the compound. The effect of the methyl group diminishes as the total complexity increases. In number (8) the combined effect of complexity and the  $\text{C}_2\text{H}_5$  group is to produce a negative difference, but in number (7) the



expanding influence of the  $\text{CH}_3$  group is sufficiently great to convert this into a positive difference. It is extremely probable that were complexity alone operative, the relative volumes would steadily diminish to a minimum at the first member of the series. Seeing, however, that the first members in each series include the methyl and ethyl groups, there is a contrary or expanding influence which is a maximum at the first member of each series, and this more than balances the effect of diminishing complexity.

### The Aldehydes.

It is evident, as Kopp himself discovered, that the aldehydes possess similar volumes to those of the paraffins, so that  $:\text{O}$  may be supposed to occupy as much space as two volumes of hydrogen.

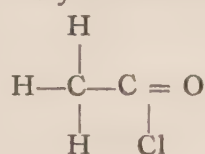
TABLE LIX.

The Aldehydes.		$V_m$ .	$V_m$ .	The Paraffins.
Acetaldehyde	$\text{CH}_3 \cdot \text{CHO}$	56.7	—	$\text{C}_2\text{H}_6$
Propaldehyde	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHO}$	74.8	—	$\text{C}_3\text{H}_8$
Butyraldehyde	$\text{C}_3\text{H}_7 \cdot \text{CHO}$	96.0	96.0	$\text{C}_4\text{H}_{10}$
Valeraldehyde	$\text{C}_4\text{H}_9 \cdot \text{CHO}$	118.2	117.8	$\text{C}_5\text{H}_{12}$
Benzaldehyde	$\text{C}_6\text{H}_5 \cdot \text{CHO}$	118.4	118.2	$\text{C}_6\text{H}_5 \cdot \text{CH}_3$

$$[:\text{O}] = 7.4.$$

The two series are strikingly similar, so that we may suppose that the volumes of the simpler paraffins resemble those of the aldehydes.

Acetyl chloride  $\text{CH}_3 \cdot \text{COCl}$



$V_m$  74.1

$\text{CH}_3$  26.0

$\text{C}$  14.8

$\text{Cl}$  22.2

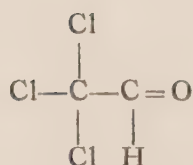
$\text{O}''$  11.0

$\Sigma_n V_d = 74.0$

$V_m = \underline{\underline{74.1}}$

Chloral  $\text{C}_2\text{Cl}_3\text{HO}$ .

$V_m$  106.37.



$V$   $\text{CCl}_3\text{H}$  84.5

less  $\text{H}$  - 3.7

80.8

$\text{CHO}$  25.9

$\Sigma_n V_d$  106.7

$V_m$   $\underline{\underline{106.37}}$

Trichloroacetyl chloride $C_2Cl_4O$ .		$V_m = 125.5$ .
$  \begin{array}{c}  \text{Cl} \\    \\  \text{Cl} - \text{C} - \text{C} = \text{O} \\    \quad   \\  \text{Cl} \quad \text{Cl}  \end{array}  $	V	$\text{CCl}_3$ 80.8
		C 14.8
		O'' 11.1 as in $-\text{CO}''\text{Cl}$
		Cl 22.2
		<hr/>
	$\Sigma_n V_a$	128.9
less for $\alpha\beta$ subst.		- 3.1
		<hr/>
	$\Sigma_n V_a$	125.8
	$V_m$	125.5
		<hr/>

### The Ketones.

Acetone  $\text{CH}_3-\text{CO}-\text{CH}_3$   $V_m$  77.1.

The volume is considerably larger than that of the isomeric propaldehyde, from which we might conclude that the volume is  $[:\text{O}] = 7.4 + 2.3 = 9.7$ .

The following methyl ketones, except the third and fourth which are interpolated, have been investigated by Thorpe.

TABLE LX.  
THE METHYL KETONES.<sup>44</sup>

Compound.	$V_m$ .	$V_m$ .	The Paraffins.
$\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3$	96.7	96.0	$\text{C}_4\text{H}_9$
$\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{CH}_3$	118.3	117.8	$\text{C}_5\text{H}_{12}$
$\text{C}_4\text{H}_9 \cdot \text{CO} \cdot \text{CH}_3$	(140.1)	139.9	$\text{C}_6\text{H}_{14}$
$\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{CH}_3$	(162.8)	162.6	$\text{C}_7\text{H}_{16}$
$\text{C}_6\text{H}_{13} \cdot \text{CO} \cdot \text{CH}_3$	186.6 (Sch.)	186.3	$\text{C}_8\text{H}_{18}$

The volumes of these methyl ketones are a little larger than those of the corresponding paraffins.

Pinacolin $\text{C}_6\text{H}_{12}\text{O}$ .		$V_m$ 138.5.
$  \left. \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \right\} \text{C} \cdot \text{CO} \cdot \text{CH}_3  $	$\text{C}_6\text{H}_{12}$	132.4
	O	7.4
		<hr/>
	$\Sigma_n V_a$	139.8
less for $\text{>}$ group		- 1.2
		<hr/>
		- 138.6
		<hr/>

$\Sigma_n V_a$  for pinacolin  $\text{C}_6\text{H}_{12}\text{O}_2$  (139.8) is not far from that of  $\text{C}_6\text{H}_{14}$  nor from that for  $\text{C}_4\text{H}_9 \cdot \text{CO} \cdot \text{CH}_3$  the normal compound.

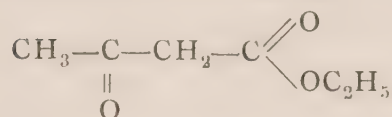
The value of the group  $\text{>}$  is about equal to two iso groups.

Since  $\text{CH}_3 \cdot \text{COCl}$  represents the acetyl group + a chlorine atom we see that  $:\text{O}$  may possess a volume larger than 7.4, one in fact equal or nearly equal to 11.0.

An interesting case is that of

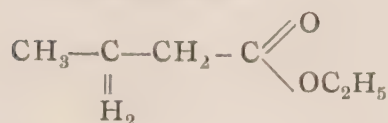
Acetoacetic ester  $C_6H_{10}O_3$ .

$V_m$  153.6



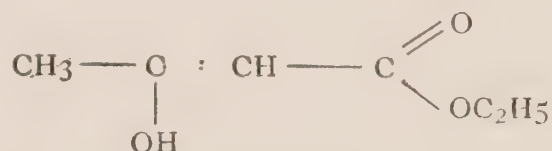
The compound has

$V_m$  150.5



$\Delta + 3.1$

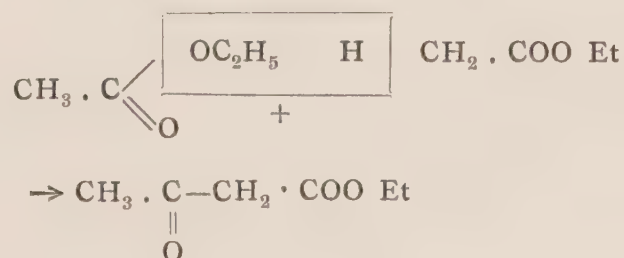
If the constitution of acetoacetic ester were "enolic"



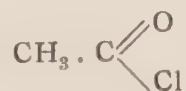
the volume would be similar to that of ethyl butyrate, or even less as the matter stands, the constitution cannot be other than "ketonic".

This is interesting from a chemical stand-point, and confirms the conclusions derived from other sources, both chemical and physico-chemical.

There is one point which may have an important bearing upon unexplained variations in atomic volumes from the normal when we form a more or less complex substance by the union or condensation of two simpler ones, one particular atom of which has a definite value in one compound, and remains unaltered in the complex one. Thus in the synthesis of aceto-acetic ester:—



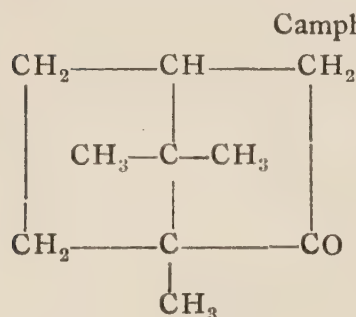
The atom  $O''$  is thus similar to carboxylic oxygen in ethyl acetate, and is also similar to the atom in:—



The group— $CH_3 \cdot CO$  is really an acetyl group and  $O''$  only apparently resembles a ketonic oxygen.



One other compound remains, also interesting, from a chemical point of view, viz. Camphor  $C_{10}H_{16}O$ .

Camphor  $C_{10}H_{16}O$ . $V_m$  187.7.

We can obtain its value from that of borneol  $C_{10}H_{18}O$   $V_m$  190.5.

$$\text{Group OH} = 6.0 + 3.7 = 9.7$$

$$C_{10}H_{16} = 190.5 - 9.7 = 180.8$$

less H 3.7

$$O'' \quad \begin{array}{r} 177.1 \\ 11.0 \end{array}$$

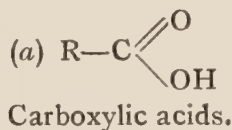
$$\Sigma_n V_a = 188.1$$

$$C_{10}H_{16}O'' \quad \begin{array}{r} 57 \times 3.7 \\ \text{less for ring} \end{array} \quad \begin{array}{r} 218.3 \\ - 30.0 \end{array}$$

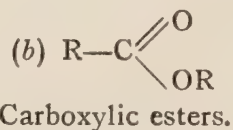
$$\begin{array}{r} \Sigma_n V_a \quad 188.3 \\ \text{Obs.} \quad 187.7 \end{array}$$

### The Carboxylic Acids.<sup>45</sup>

The *aldehydes* and *ketones* give rise to the



and



These compounds contain the oxygen atom  $\cdot O \cdot$  and the doubly-bound one  $:O$ .

TABLE LXI.

Substances.	$V_m$ .	$nCH_2$ .	$\Delta$ for $O_2$ .
Propionic . . . $C_3H_6O_2$	85.3	66.3	19.0
Butyric . . . $C_4H_8O_2$	107.8	88.4	19.4
Valerianic . . . $C_5H_{10}O_2$	130.0	110.5	19.5
Caproic . . . $C_6H_{12}O_2$	152.5	132.6	19.9
Heptoic . . . $C_7H_{14}O_2$	174.6	155.6	19.4
Mean value =			19.5

These acids are altogether exceptional, in that, although they contain the hydroxyl group, their volumes are by no means diminished in consequence.

The value of : O may be obtained as follows :—

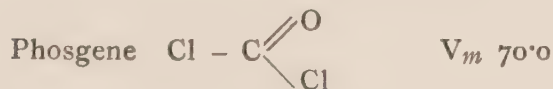
TABLE LXII.

The Fatty Acids.	V <sub>m</sub> .	O''.	V <sub>m</sub> .	The Paraffins.
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> . .	85·3	11·3	74·0	C <sub>3</sub> H <sub>8</sub>
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> . .	107·8	11·8	96·0	C <sub>4</sub> H <sub>10</sub>
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub> . .	130·0	12·2	117·8	C <sub>5</sub> H <sub>12</sub>
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> . .	152·5	12·6	139·9	C <sub>6</sub> H <sub>14</sub>
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> . .	174·6	12·0	162·6	C <sub>7</sub> H <sub>16</sub>

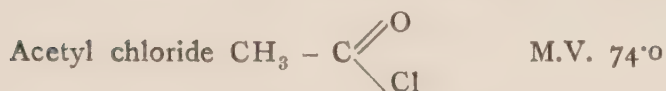
The average value of O'' is 12·0, the assumption being that

$$\begin{aligned} [\cdot O \cdot] &= 2H \\ \text{for } [O''] + [O'] &= 12 \times 7\cdot4 = 19\cdot4. \end{aligned}$$

The value of O'' can also be obtained from the compounds containing the group  $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{Cl} \end{smallmatrix}$ .

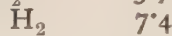
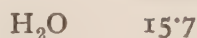


$$O'' = 74\cdot0 - (14\cdot8 + 2 \times 22\cdot1) = 11\cdot0$$



$$O'' = 74\cdot0 - (14\cdot8 + 25\cdot9 + 22\cdot1) = 11\cdot3$$

From acetic anhydride we obtain the value of O'



$$O'' + O' = 11\cdot3 + 8\cdot3 = 19\cdot6.$$

The excess is thus thrown on to the O'' or on to the O' according to the method of calculation.

The simplest explanation is to suppose that [O''] = 3[H] and [O'] = 2[H].

Then, assuming that O<sub>2</sub> = 19·5

$$[O''] = 11\cdot7 \quad \text{and} \quad [O'] = 7\cdot8.$$

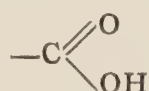
### The Methyl Esters.<sup>46</sup>

The methyl esters are sharply distinguished as regards the volumes of oxygen from the acids on the one hand, and from the more symmetrical esters on the other.

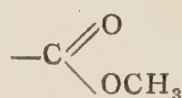
TABLE LXIII.

Radicles.	<i>The Acids.</i>		<i>The Methyl Esters.</i>		<i>Symmetrical.</i>	
	<i>V<sub>m</sub>.</i>	$\Delta$ .	<i>V<sub>m</sub>.</i>	$\Delta$ .	<i>V<sub>m</sub>.</i>	
CH <sub>3</sub> —CO—	85.3	-2.1	83.2	+1.4	84.6	H . CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
C <sub>2</sub> H <sub>5</sub> —CO—	107.8	-3.2	104.6	+1.5	106.1	CH <sub>3</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>
C <sub>3</sub> H <sub>7</sub> —CO—	130.0	-3.3	126.7	+1.7	128.4	CH <sub>3</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>
C <sub>4</sub> H <sub>9</sub> —CO—	152.5	-3.4	149.1	+1.4	150.5	C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>
C <sub>5</sub> H <sub>11</sub> —CO—	174.6	-2.4	172.2	+1.8	174.0	C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>
Mean =		-2.9	Mean =		+1.6	

We find that by comparing—

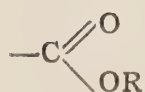


and

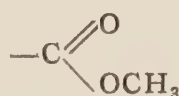


$$\Delta - 2.9$$

and also



and



$$\Delta + 1.6.$$

This result is quite different from that shown by the alcohols CH<sub>2</sub> . OH, as compared with CH<sub>2</sub> O . CH<sub>3</sub> and CH<sub>2</sub>—O—R.

The alcohols are depressed, whilst the acids are augmented in volume.

As regards the ethers and esters, the O—CH<sub>3</sub> group produces a diminution in volume in both.



TABLE LXIV.

## MONOCARBOXYLIC ESTERS.

(Second Series.)

Substances.	$V_m$ .	$n\text{CH}_2(22\cdot1)$ .	$\text{O}_2$ .
$\text{HCO}_2\text{CH}_3$ . . . .	62·6	44·2	18·4
$\text{HCO}_2\text{C}_2\text{H}_5$ . . . .	84·8	66·3	18·5
$\text{H} \cdot \text{CO}_2\text{C}_3\text{H}_7$ . . . .	106·4	88·4	18·0
$\text{CH}_3 \cdot \text{CO}_2\text{C}_3\text{H}_7$ . . . .	128·8	110·5	18·3
$\text{C}_2\text{H}_5 \cdot \text{CO}_2\text{C}_3\text{H}_7$ . . . .	151·0	132·6	18·4
Mean value			= 18·3

TABLE LXV.

The Esters. $\text{C}_n\text{H}_{2n}\text{O}_2$ .	$V_m$ .	$\text{O}''$ .	$V_m$ .	The Paraffins. $\text{C}_n\text{H}_{2n+2}$ .
$\text{HCO}_2\text{CH}_3$ . .	62·6	11·0	51·6	$\text{C}_2\text{H}_6$
$\text{HCO}_2 \cdot \text{C}_2\text{H}_5$ .	84·8	10·8	74·0	$\text{C}_3\text{H}_8$
$\text{H} \cdot \text{CO}_2 \cdot \text{C}_3\text{H}_7$ .	106·4	10·4	96·0	$\text{C}_4\text{H}_{10}$
$\text{CH}_3 \cdot \text{CO}_2 \cdot \text{C}_3\text{H}_7$	128·8	11·0	117·8	$\text{C}_5\text{H}_{12}$
$\text{C}_2\text{H}_5 \cdot \text{CO}_2 \cdot \text{C}_3\text{H}_7$	151·0	11·1	139·9	$\text{C}_6\text{H}_{14}$
Mean = 10·9				

Thus assuming that  $[\cdot \text{O}' \cdot] = 7\cdot4$  ( $2\text{H}$ )  $[\text{O}''] = 10\cdot9$   
 $[\text{O}'] + [\text{O}''] = 7\cdot4 + 10\cdot9 = 18\cdot3$ .

We thus have—

for the acids . . . .	$\text{O}_2$	19·5	$\text{O}''$	11·7	$\text{O}'$	7·8
the methyl esters . .	$\text{O}_2$	16·6	$\text{O}''$	11·0	$\text{O}'$	5·6
and the symmetrical esters .	$\text{O}_2$	18·3	$\text{O}''$	11·0	$\text{O}'$	7·4

There is distinct evidence that  $[\text{O}''] = 3\text{H}$  and  $[\text{O}'] = 2\text{H}$  throughout the series, in the following :—

TABLE LXVI.

SYMMETRICAL.

Esters.	V <sub>m</sub> .	V <sub>m</sub> .	Ethers.
C <sub>n</sub> H <sub>2n</sub> O <sub>2</sub>			C <sub>n</sub> H <sub>2n+2</sub> O
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	62·6	62·5	C <sub>2</sub> H <sub>6</sub> O
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	84·8		C <sub>3</sub> H <sub>8</sub> O
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	106·4	106·4	C <sub>4</sub> H <sub>10</sub> O
C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	128·8	128·0	C <sub>5</sub> H <sub>12</sub> O
C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	151·0	151·3	C <sub>6</sub> H <sub>14</sub> O
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	174·6	174·7	C <sub>7</sub> H <sub>16</sub> O
C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	197·7	197·7	C <sub>8</sub> H <sub>18</sub> O
C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	221·9	221·1	C <sub>9</sub> H <sub>20</sub> O
C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	245·9	246·1	C <sub>10</sub> H <sub>22</sub> O
C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	270·3	271·3	C <sub>11</sub> H <sub>24</sub> O
C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	295·9	295·5	C <sub>12</sub> H <sub>26</sub> O
C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	351·2	353·4	C <sub>14</sub> H <sub>30</sub> O
C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	377·0	377·6	C <sub>15</sub> H <sub>32</sub> O
C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	404·3	404·5	C <sub>16</sub> H <sub>34</sub> O

Thus, in spite of the change due to complexity

$$[O'] = 2[H] \text{ and } [O''] = [>O] = 3[H]$$

under ordinary conditions  $[O'] = 7·4$   $[O''] = [>O] = 11·0$ . In both series we find contractions when the group  $-OCH_3$  is present. (a) A diminution of about  $-1·0$  in the ethers and (b) a diminution of  $-1·8$  in the esters. This may be due to a contraction of the O' atom alone, of the whole group, or of only the  $CH_3$  group under the influence of the oxygen atom.

### The Effect of the Homologous Increment $CH_2$ on the Volumes of the Monocarboxylic Esters.

These compounds have been studied chiefly by Gartenmeister (loc. cit.), Schiff, and Elsässer.

The series of the methyl esters may be made use of to illustrate Lossen's method of calculating the volumes of series of compounds.

Thus, the volume of methyl formate  $HCOOCH_3$  is  $V_m$  62·7, and the difference between this volume and that of methyl acetate  $CH_3 \cdot COOCH_3$  is  $\Delta = 20·5$ .

The assumption is made that the volume of the homologous increment  $CH_2$  increases by 0·5 from term to term.

Thus for any compound  $C_nH_{2n}O_2$

$$V_m = 62·7 + (n - 2) 20·5 + 0·5 \frac{(n - 2)^2}{2} \quad . \quad . \quad . \quad (1)$$

Now Kopp had made the assumption that

$$[H_2] = [O], \text{ (for both } O' \text{ and } O'')$$

and this, combined with the assumption that the average initial difference for  $CH_2$ , is

$$\Delta CH_2 = 20.9$$

enabled Lossen to calculate from methyl formate

$$\begin{array}{l} C_2H_4O_2 \quad . \quad V_m = 62.7 \\ \text{the values } [C] = 10.45 \quad [H] = 5.225 \quad [O] = 10.45 \end{array}$$

Then the above equation becomes

$$V_m = 10.45n + 5.225m + 10.45O + 0.25(n - 2)^2,$$

and by its aid, the volumes of the different members of the series can be calculated.

A different method is adopted here, which is based on the idea that whatever may be the changes in volume in a homologous series, the relative volumes remain the same throughout.

If we assume that

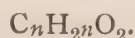
$$C = 4H, O' = 2H, O'' = 3H$$

in the formic esters, we may obtain a curve which shows how the atomic volumes change throughout the homologous series. This is accomplished by finding the sum of the hydrogen equivalents in the different compounds, and the quotient of the volume  $V_m$  and this sum  $W$ , gives the volume of hydrogen in a particular compound. By this means we avoid the necessity of making use of the difference in volume between two consecutive members of a series, which is neither true for the one compound nor the other.

Thus for compound  $C_nH_{2n}O_2$

$$V_m = (6n + 5)S = WS.$$

TABLE LXVII.—VOLUMES OF THE ATOMS IN THE FORMIC ESTER SERIES.



Compound.	W.	$V_m$ .	$\frac{V_m}{W}$ .
Methyl formate . $HCO_2CH_3$	17	62.7	3.688
Ethyl       " $HCO_2C_2H_5$	23	84.6	3.678
Propyl      " $HCO_2C_3H_7$	29	106.2	3.666
Butyl       " $HCO_2C_4H_9$	35	127.6	3.645
Amyl        " $HCO_2C_5H_{11}$	41	150.5	3.671
Hexyl       " $HCO_2C_6H_{13}$	47	173.3	3.688
Heptyl      " $HCO_2C_7H_{15}$	53	196.7	3.711
Octyl        " $HCO_2C_8H_{17}$	59	220.3	3.734

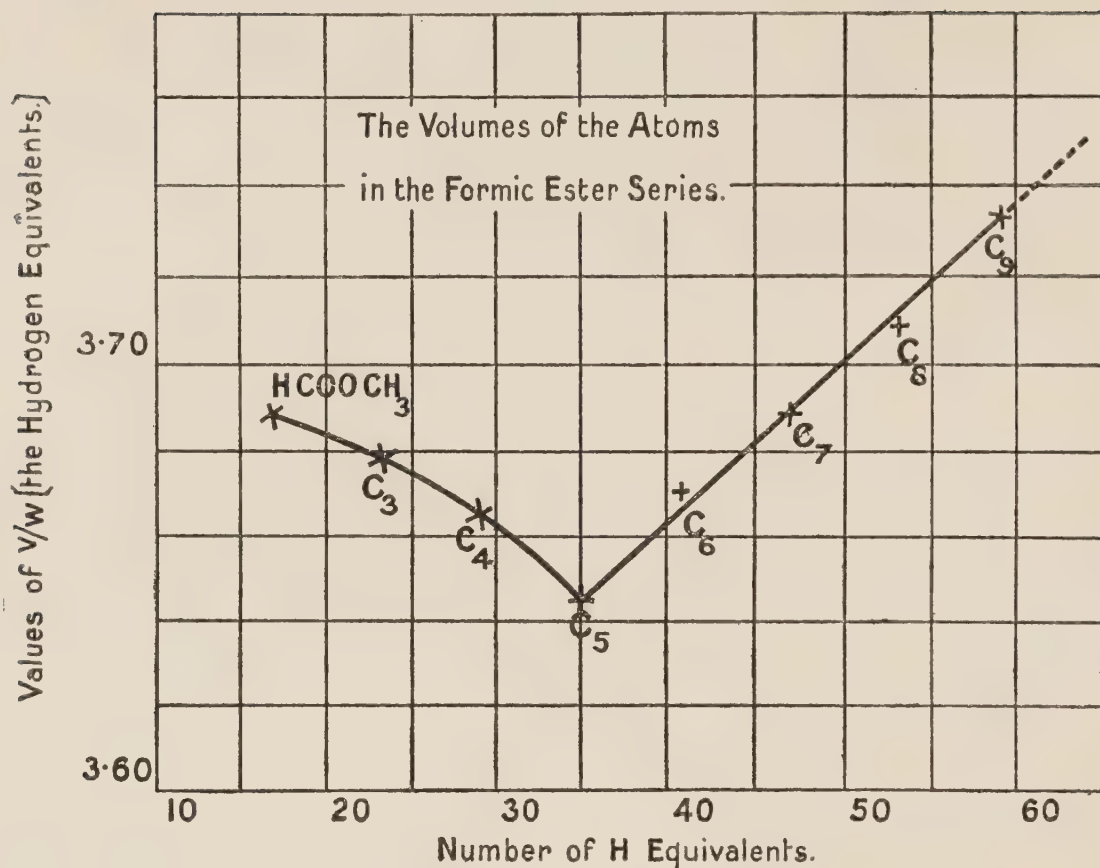


FIG. 6.

The above curve shows how the volumes of the atoms, and thus of the group  $\text{CH}_2$ , vary in the formic ester series.

The curve is very similar to the methyl ether curve, and shows a well-marked region of diminishing values of  $V/W$ . The region of the minimum is here reduced to a point, as the curve is formed by the intersection of two others. The ascending curve is as far as we can make out linear, with a value of  $\Delta V/W = 0.022$  on the average. The curve as a whole, whilst in many respects resembling that for the normal paraffins, is in others quite different.

These curves do not seem capable of exact mathematical formulation, but this is not of great consequence, as the molecular volumes of compounds are calculated in quite a different way. It is much better to consider the total variation from a volume calculated from mean values, and regard this total variation as due to general or particular constitutive influences. An estimation of the values of these is often possible. The curves are, however, useful in showing how the atomic volumes vary in a series, and also in indicating points of similarity or contrast with the curves for other series.



So far as the methyl ester series is concerned, we find that—

$$S' = 3.645 + (\overline{6n + 5 - 35}) \times 0.0037$$

since  $1/6$  of  $0.0022$  is  $= 0.0037$

and the total volume of a compound is

$$V_m = (6n + 5) \{3.645 + (6n - 30) \times 0.0037\}.$$

If we compare the volumes of certain of these compounds, we get the following constants:—

H . COOCH <sub>3</sub>	$V_m$ 62.70
H . COOC <sub>6</sub> H <sub>13</sub>	$V_m$ 173.30
5CH <sub>2</sub> 110.6	CH <sub>2</sub> 22.12
Since H . COOCH <sub>3</sub> is C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	
O <sub>2</sub> = 62.70 - 44.24 = 18.46	
Now	$\left. \begin{array}{l} O' \quad 7.4 \\ O'' \quad 11.1 \end{array} \right\} 18.5 \text{ for } O_2 \quad CH_2 = 22.1.$

Although the results obtained by Lossen's method and the one just described are both in good accord with the experimental results, yet there are some points of difference between them.

The most important of these is the difference in the curves representing the atomic volumes in different members of the series.

Lossen assumes that the expansion is rectilinear from the first compound, whereas the curve just indicated shows a contraction to a minimum at the fourth member and then an expansion. In this respect the methyl ester curve is similar to all the other curves studied.

### The Methyl, Ethyl, and Propyl Salts of the Fatty Acids.

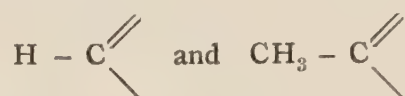
This is an arrangement of the esters which is quite different from the other. In the first, the acid is the same, but the alkyl groups are different; in this arrangement the fatty acid radicles are different, but the alkyl group is the same for all. It by no means follows that the relations between the atomic volumes are the same in the two methods of arrangement. It has been found that better results and smoother curves are obtained by utilizing Schiff's data as well as those of Gartenmeister. The methyl ester curve is wholly from Gartenmeister's results, the ethyl ester curve is partly due to Schiff and partly to Gartenmeister, whilst all the values employed in the formation of the

propyl curve are due to Gartenmeister except that for propyl propionate.

We give below a diagram showing the volumes of the esters of formic and acetic acids. There is a very great difference between the first part of the two curves. On comparing the formulæ



we see that this difference is to some extent connected with the different effects of the two groups



The  $\text{CH}_3$  group again is responsible for a contraction. It is, however, difficult to analyse the data completely, because at this point the effect and change due to complexity is enormous. The best results are obtained if we can compare the volumes of different compounds of similar complexity. Some of these effects are very complex, and are the sum total of the combined effects of the atoms and groups.

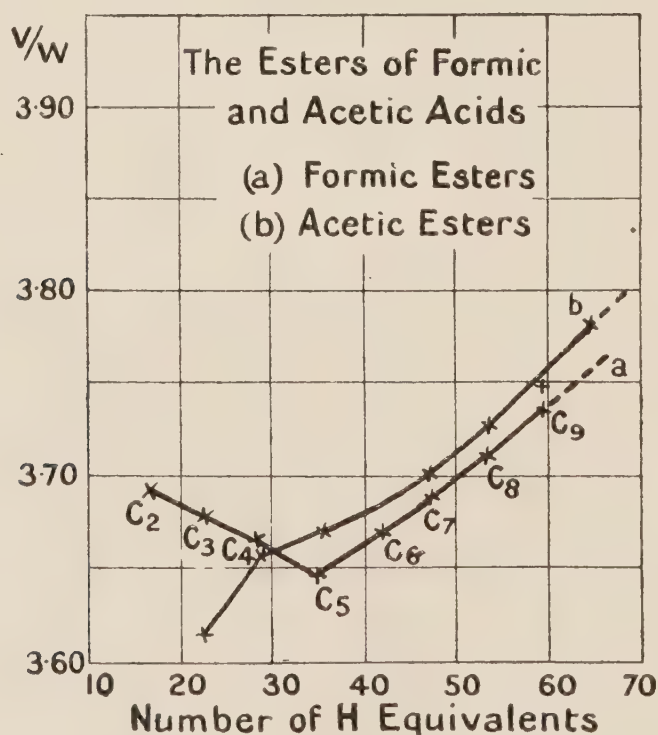


FIG. 7.

TABLE LXVIII.—METHYL, ETHYL, AND PROPYL SALTS OF THE FATTY ACIDS.

Methyl Salts.				Ethyl Salts.				Propyl Salts.			
W	Compounds.	V <sub>m</sub> .	V/W.	W	Compounds.	V <sub>m</sub> .	V/W.	W	Compounds.	V <sub>m</sub> .	V/W.
17	H . CO <sub>2</sub> . CH <sub>3</sub>	62.7	3.688	23	H . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	84.7	3.683	29	H . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	106.2	3.662
23	CH <sub>3</sub> . CO <sub>2</sub> . CH <sub>3</sub>	83.8	3.617	29	CH <sub>3</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	106.1	3.656	35	CH <sub>3</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	128.4	3.668
29	C <sub>2</sub> H <sub>5</sub> . CO <sub>2</sub> . CH <sub>3</sub>	104.6	3.607	35	C <sub>2</sub> H <sub>5</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	128.1	3.660	41	C <sub>2</sub> H <sub>5</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	151.0	3.683
35	C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> . CH <sub>3</sub>	126.7	3.620	41	C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	150.5	3.670	47	C <sub>3</sub> H <sub>7</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	174.0	3.702
41	C <sub>4</sub> H <sub>9</sub> . CO <sub>2</sub> . CH <sub>3</sub>	149.1	3.636	47	C <sub>4</sub> H <sub>9</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	—	—	53	C <sub>4</sub> H <sub>9</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	197.8	3.732
47	C <sub>5</sub> H <sub>11</sub> . CO <sub>2</sub> . CH <sub>3</sub>	172.2	3.664	53	C <sub>5</sub> H <sub>11</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	—	—	59	C <sub>5</sub> H <sub>11</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	222.2	3.766
53	C <sub>6</sub> H <sub>13</sub> . CO <sub>2</sub> . CH <sub>3</sub>	196.2	3.702	59	C <sub>6</sub> H <sub>13</sub> . CO <sub>2</sub> . C <sub>2</sub> H <sub>5</sub>	—	—	65	C <sub>6</sub> H <sub>13</sub> . CO <sub>2</sub> . C <sub>3</sub> H <sub>7</sub>	246.5	3.792
59	C <sub>7</sub> H <sub>15</sub> . CO <sub>2</sub> . CH <sub>3</sub>	220.1	3.730								

In the above table, we notice the general effect of change of complexity on the atomic volumes, and this is also indicated by the curves. These curves are totally unlike those shown to be applicable to the esters of the same acid. They, however, resemble the curves for the normal paraffins and other compounds. (a) The descending portion is more pronounced for

the methyl salts than for the others, for the reason that the simplest compounds of the series have shorter chains, and are in general of smaller complexity. (b) The curves are wide and open, especially that for the methyl salts. This is totally unlike the curve for the methyl ethers or for the esters of formic acid which are broken at the minimum, owing to an abrupt change in the curvature.

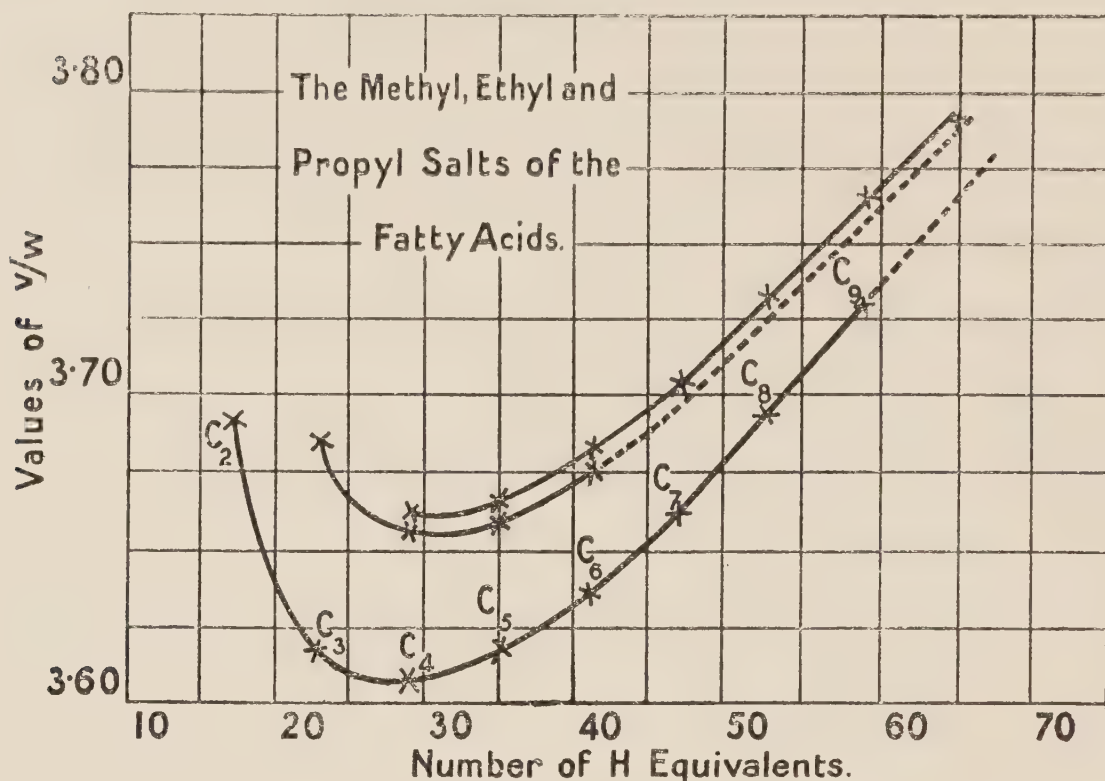
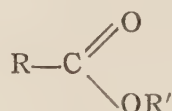


FIG. 8.

### An Examination of the Causes of the Variation of the Volumes of Isomers, and a Consideration of the General Question of the Influence of Symmetry.

It was shown by Gartenmeister that the volumes of compounds possessing similar formulæ, but differing in the method of the distribution of the carbon atoms between the O and C radicals, possess somewhat different volumes. Thus in a compound



R and R' may have different complexities, and the volumes of the compounds depend on this circumstance to some extent. Similarly the boiling-points vary.

The following series shows this.



TABLE LXIX.—THE ISOMERIC ESTERS OF FORMULA  $C_8H_{16}O_2$ .

Compound.	$V_m$ .	b.p.
$C_6H_{13} \cdot COOCH_3$	196.2	173.0
$C_5H_{12} \cdot COOC_2H_5$	197.7	167.0
$C_4H_{11} \cdot COOC_3H_7$	197.8	167.0
$C_3H_7 \cdot COOC_4H_9$	197.8	165.7
$CH_3 \cdot COOC_6H_{13}$	197.7	169.0
$H \cdot COOC_7H_{15}$	196.7	176.0

The volumes are seen to be a minimum at the extremities of the series, and a maximum at the centre. The opposite is true of the boiling-points.

This has been ascribed to differences in the symmetry of the molecules. Compounds in which the radicles differ most, possess the smallest volumes, and those in which they are most nearly equal possess the largest volumes. The latter are the most symmetrical compounds, and the former the least symmetrical. We believe that a consideration of such influences as symmetry, which are incapable of accurate measurement, is undesirable and that it will be better to substitute considerations of the specific influences of groups.

*Influence of the C and O Groups.*

In the above compounds the groups



produce contractions of  $-1.6$  and  $-1.1$  respectively. The former group is a frequent cause of contraction in volume as will be seen from Table LXVIII on the methyl and ethyl esters. The mean difference between the volumes of methyl esters and those of the corresponding ethyl and propyl compounds is  $-1.6$ , a number which is exactly similar to the one just given. The volumes of the methyl esters are thus below the normal, whilst it may be shown that the symmetrical compounds are normal.

Thus for

$HCO_2C_2H_5$	$V_m$	84.6
$C_2H_5$		48.0
$CO_2$		33.3
$H$		3.7
		<hr/>
$\Sigma_n V_a$		85.0
$V_m$		84.5
		<hr/>

The volume of



is thus  $1.4$  below the normal.

This is no doubt due to the methyl group, since a similar feature is noticed in the case of other methyl compounds.

It is, however, necessary to also take into consideration other groups in a compound, and possible interactions.

Thus in the salts of formic acid we note the following

H . CO <sub>2</sub> CH <sub>3</sub>	V <sub>m</sub>	62.7	17 × 3.7 = 62.9	Δ	- 0.2
H . CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>		84.6	23 × 3.7 = 85.1	Δ	- 0.5
H . CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub>		106.2	29 × 3.7 = 107.3	Δ	- 1.1
H . CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>		127.6	35 × 3.7 = 129.5	Δ	- 1.9
H . CO <sub>2</sub> C <sub>5</sub> H <sub>11</sub>		150.5	41 × 3.7 = 151.7	Δ	- 1.2
H . CO <sub>2</sub> C <sub>6</sub> H <sub>11</sub>		173.3	47 × 3.7 = 173.9	Δ	- 0.6

Thus the contraction increases as the group increases, up to a certain point, and then diminishes. (See also curve.)

These effects are no doubt complex, and the exact analysis of the data is difficult. Much depends on the exact configuration of the molecules, and the particular groups acting. The first is a subject about which comparatively little is known. Another of the complications is, as already shown, the influence of symmetry.

It will be noted that the series

(a) R—COOH	aliphatic acids	Δ
(b) R—COOCH <sub>3</sub>	methyl esters	
(c) R—COOC <sub>2</sub> H <sub>5</sub>	ethyl esters	
· · · · ·		
R—COOR'	higher esters.	

are truly homologous series, if we are to judge by the constancy of the differences Δ between the corresponding members of pairs of series.

On the other hand, if we arrange the substances as different salts of the same acid, complications are introduced, if we are to judge by the variable character of the differences Δ. For this reason, these series are not regarded as truly homologous. By the first method of arrangement, we notice that the group CH<sub>3</sub>, attached to the atom O, is responsible for a constant difference Δ = - 1.6, and is thus independent of the complexities of the compounds. Similarly, the group C<sub>2</sub>H<sub>5</sub> is found to be responsible for a smaller diminution. By comparing the volumes of isomeric compounds we notice this depressing influence of CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc., both when attached to the O radical and the C radical, and moreover the amount of the contraction can be estimated. This method gets rid of the complicating influence of complexity.

Any depressing influence of particular groups is also revealed by an examination of the curves.

We obtain similar results from an examination of the dicarboxylic esters,<sup>47</sup> but the depressions are comparatively small.

Compounds :	V.	$n\text{CH}_2$ .	$\text{O}_2$ .
Methyl oxalate ( $\text{COOCH}_3$ ) <sub>2</sub>   $\text{COOCH}_3$	117.4	81.0	$2 \times 18.2$
$\text{COOC}_2\text{H}_5$	139.6	103.2	$2 \times 18.2$

The groups  $\text{COOCH}_3$ ,  $\text{COOC}_2\text{H}_5$  have elsewhere been found to be equal to 59.0 and 80.9 respectively. The numbers would give to

( $\text{COOCH}_3$ ) <sub>2</sub>	the volume of $2 \times 59.0$	118.0	$\Delta = -0.6$
and $\text{COOCH}_3$	the volume of $59.0 + 80.9$	139.9	$\Delta = -0.3$
$\text{COOC}_2\text{H}_5$			

(See Appendix 2, p. 264.)

### The Unsaturated Oxygen Compounds.<sup>48</sup>

Acrolein $\text{CH}_2 : \text{CH} \cdot \text{C} \begin{array}{l} \text{O} \\ \text{H} \end{array}$	
b.p. 52.4	$d_{20} 0.8410$
$\text{C} = 0.50$	$V_m 69.9.$
	$V_m.$
Propaldehyde $\text{CH}_3 \cdot \text{CH}_2 \text{C} \begin{array}{l} \text{O} \\ \text{H} \end{array}$	74.8
$2\text{H}$	7.4
$\text{CH}_2 : \text{CH} \cdot \text{C} \begin{array}{l} \text{O} \\ \text{H} \end{array}$	67.4
$\Delta = 69.9 - 67.4 = + 2.5.$	

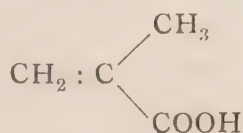
There is thus an augmentation due to unsaturation.

There are no data for acrylic acid, but Weger has studied the esters of this acid.

Methyl acrylate $\text{CH}_2 : \text{CH} \cdot \text{COOCH}_3$	
b.p. 80°.	$V_m 98.6$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOCH}_3$	104.6
$\text{CH}_2 : \text{CH} \cdot \text{COOCH}_3$	97.2
$\Delta = 98.6 - 97.2 = + 1.4.$	

There is again an increase for unsaturation.

It is remarkable that a methyl acrylic acid



should possess a similar volume, viz. 98.4.

C.	Unsaturated esters : Methyl acrylate, etc.	$V_m$ .	Sat. Est.	$-H_2 = \Sigma_n V_a$ .	$\Delta$
0.515	$CH_2 : CH . COOCH_3$	98.6	104.6 (G)	97.2	+ 1.4
0.595	$CH_2 : CH . COOC_2H_5$	122.0	128.1 (S)	120.7	+ 1.3
0.551	$CH_2 : CH . COOC_3H_7$	145.3	151.0 (S)	143.6	+ 1.7

There is thus seen to be the same augmentation for all these compounds. This is considered to be due to unsaturation, or rather to the result of an interaction between an unsaturated group and an ethenoid linkage.

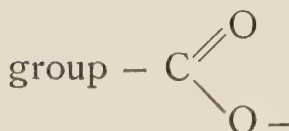
The volume of the isomeric allyl acetate



Propyl acetate  $CH_3 . CO . OCH_2 . CH_2 . CH_3$

$V_m$	128.9
$- H_2$	7.4
$\Sigma_n V_a$	121.5
$V_m$	<u>121.7</u>

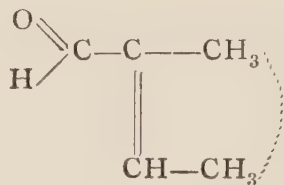
There is no augmentation in this case, because the ethenoid linkage is out of the range of the influence of the unsaturated



It has already been pointed out that the vinyl derivatives (p. 88)  $CH_2 : CHX$ , etc., show the same augmentation.

Tiglic aldehyde

$CH_3 . CH : C(CH_3) . CHO$		
b.p. 116	$d_{15}$ 0.871	$C = 0.52$
$V_m$	109.5	
$2CH_3$	52.0	
$2CH$	37.0	
CO	22.2	
	<hr/>	
	111.2	
less for $\alpha \beta$	- 3.1	
	<hr/>	
	108.1	
for unsat.	+ 1.5	
	<hr/>	
$\Sigma_n V_a$	109.6	
$V_m$	<u>109.5</u>	



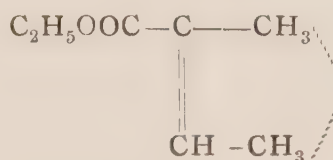
Formula of tiglic aldehyde.

Ethyl angelate

$CH_3 . CH : C(CH_3) . COOC_2H_5$	
b.p. 141	$d_0$ 0.9347
$C_7H_{12}O_2$	$CH_3 . CH_2 . CH_2 . CH_2 . COOC_2H_5$ (ethyl valerate)
	$C = 0.578$



Ethyl angelate	$V_m$ 163.9
2CH <sub>3</sub>	52
C <sub>2</sub> H <sub>5</sub>	48
COO	33.3
C <sub>2</sub> H	33.3
	<hr/>
	166.6
less for $\alpha$ $\beta$ struct.	- 3.1
	<hr/>
	163.5
for unsat.	+ 1.3
	<hr/>
$\Sigma_n V_a$	164.8
$V_m$	<u>163.9</u>

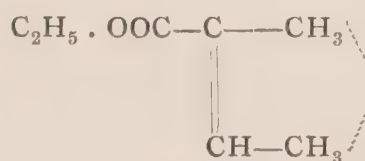


Formula of ethyl angelate.

The increase for unsaturation is in this case doubtful. This may be due to inaccuracy in the calculations.

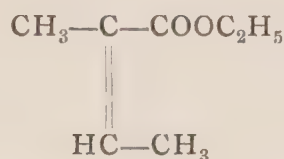
Ethyl tiglate (ethyl and methyl crotonate)

$\text{CH}_3 \cdot \text{CH} : \text{C}(\text{CH}_3) \text{COOC}_2\text{H}_5$	
b.p. 152. $d_0$ .9425.	
C = .58	$V_m$ 164.1
2CH <sub>3</sub>	52.0
C <sub>2</sub> H <sub>5</sub>	48.0
COO	33.3
C <sub>2</sub> H	33.3
	<hr/>
	166.6
less for $\alpha$ $\beta$ struct.	- 3.1
	<hr/>
	163.5
for unsat.	+ 1.3
	<hr/>
$\Sigma_n V_a$	164.8
$V_m$	<u>164.1</u>

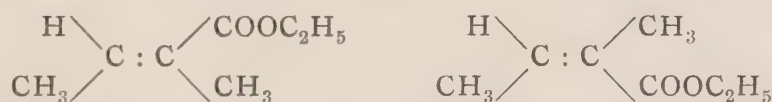


Formula of ethyl tiglate.

or



Ethyl angelate and tiglate are probably isomers of the type

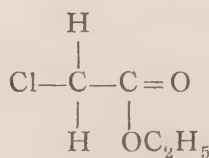


The evidence is not quite clear as to which formula represents the angelic acid derivative and which is the tiglate, owing to want of precision in the data.

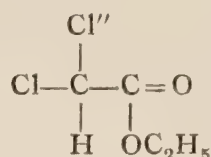
### The Substituted Esters.<sup>49</sup>

Ethyl monochloracetate

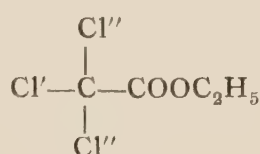
$\text{CH}_2\text{Cl} \cdot \text{COOC}_2\text{H}_5$	$V_m$ 123.9
$\text{CH}_3 \cdot \text{COOC}_2\text{H}_5$	$V_m$ 106.1
less H	- 3.7
	<hr/>
	102.4
plus Cl'	21.5
	<hr/>
$\Sigma_n V_a$	123.9
$V_m$	<u>123.9</u>



Ethyl dichloracetate		
$\text{CHCl}_2\text{COOC}_2\text{H}_5$	$V_m$	143.9
$\text{CH}_3 \cdot \text{COOC}_2\text{H}_5$	$V_m$	106.1
less $\text{H}_2$		-7.4
		<hr/>
plus $\text{Cl}'$		98.7
		+ 21.5
		<hr/>
plus $\text{Cl}''$		120.2
		23.5
		<hr/>
$\Sigma_n V_a$		143.7
$V_m$		143.9
		<hr/>



Ethyl trichloracetate		
$\text{CCl}_3 \cdot \text{COOC}_2\text{H}_5$	$V_m$	163.4
$\text{CH}_3 \cdot \text{COOC}_2\text{H}_5$	$V_m$	106.1
less 3H		-11.1
		<hr/>
plus $\text{Cl}'$		95.0
		+ 21.5
		<hr/>
plus $\text{Cl}''$		116.5
		48.0 (2 × 24.0)
		<hr/>
$\Sigma_n V_a$		164.5
$V_m$		164.4
		<hr/>



We find among the above compounds, that as the chlorine content of the substances increases, the boiling-points are diminished and the volumes augmented.

	b.p.	$\Delta$ .	$V_a(\text{Cl})$ .
$\text{CH}_2\text{Cl} \cdot \text{COOC}_2\text{H}_5$	144.5		21.5
$\text{CHCl}_2 \cdot \text{COOC}_2\text{H}_5$	157.7	13.2	22.7 × 2
$\text{CCl}_3 \cdot \text{COOC}_2\text{H}_5$	167.1	9.4	23.1 × 3

This is exactly what was noticed in the chlor-substituted methanes.

It is not easy to say whether all the chlorine atoms partake of the increase, or whether the increase is only operative on the additional carbon atoms. An explanation of the fact of increase is no doubt of fundamental importance.

We calculate the following values in order to obtain a broader basis of fact :—

C.		b.p.	$\Delta$ .	$d_{19}$ .	$V_m$ .	$V(\text{Cl})$ average.
0.540	$\text{CH}_2\text{Cl} \cdot \text{COOCH}_3$	128.5		1.2352	100.9	21.4
0.555	$\text{CHCl}_2 \cdot \text{COOCH}_3$	144.0	15.5	1.3808	120.8	22.5 × 2
0.570	$\text{CCl}_3\text{COOCH}_3$	152.5	7.5	1.4892	141.1	23.0 × 3

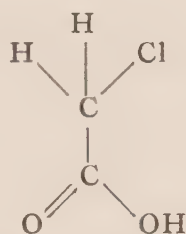
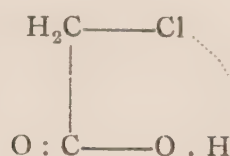
Again, we notice the phenomenon of gradually diminishing differences in boiling-points and increasing volumes as the number of chlorine atoms increases. The values may be calculated from that of methyl acetate as before.

Esters.	$\Sigma_n V_a - nH.$	+ $nCl.$	Calculated values.	$V_m.$
$CH_3 \cdot COOCH_3$	83.2			83.2
$CH_2Cl \cdot COOCH_3$	79.5	21.5	101.0	100.9
$CHCl_2 \cdot COOCH_3$	75.8	21.5 + 23.5	120.8	120.8
$CCl_3 \cdot COOCH_3$	72.1	21.5 + 48.0	141.6	141.1

A very interesting series of compounds is that of the mono-di and tri-chlor acetic acids.

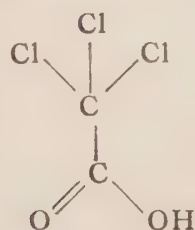
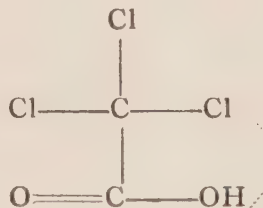
Monochloracetic acid	$CH_2Cl \cdot COOH$
b.p. 186.0	$d_{73} 1.366$ (Hoffmann).
$C = 0.530$	$V_m 78.0$
$CH_3COOH$	64.0
less H	-3.7
	<hr/>
	60.3
plus Cl	21.5
	<hr/>
$\Sigma_n V_a$	81.8
$V_m$	78.0
	<hr/>
$\Delta$	-3.8

We notice in this case a large difference of -3.8 between the two values. On examination we find that this is just what we should expect, for on writing the formula



we see that the substance is an  $\alpha\beta$  chlor-hydrin. As such, it is subject to a contraction of about -3.1.

Trichloracetic acid.	$CCl_3 \cdot COOH$
b.p. 197.0 (mean)	$d_{46} 1.617$
$C = 0.570$	$V_m 119.5$
$CH_3 \cdot COOH$	64.0
3H	-11.1
	<hr/>
	52.9
Cl'	21.5
	<hr/>
	74.4
2Cl''	48.0
	<hr/>
	122.4
less for $\alpha\beta$ structure	-3.1
	<hr/>
$\Sigma_n V_a$	119.3
$V_m$	119.5

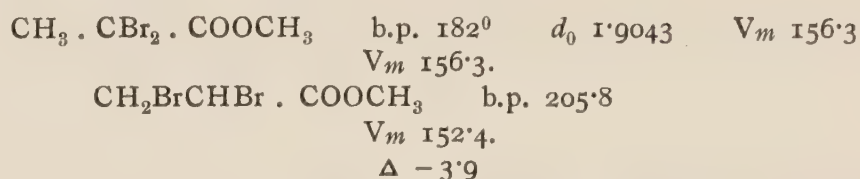


Since there is only one hydroxyl group it can influence only one chlorine atom, and so only the simple contraction  $-3.1$  is found throughout the series.

### The Dibromopropionic Esters.<sup>48</sup>

Weger has determined the volumes of a number of dibrom esters, which present some noteworthy features.

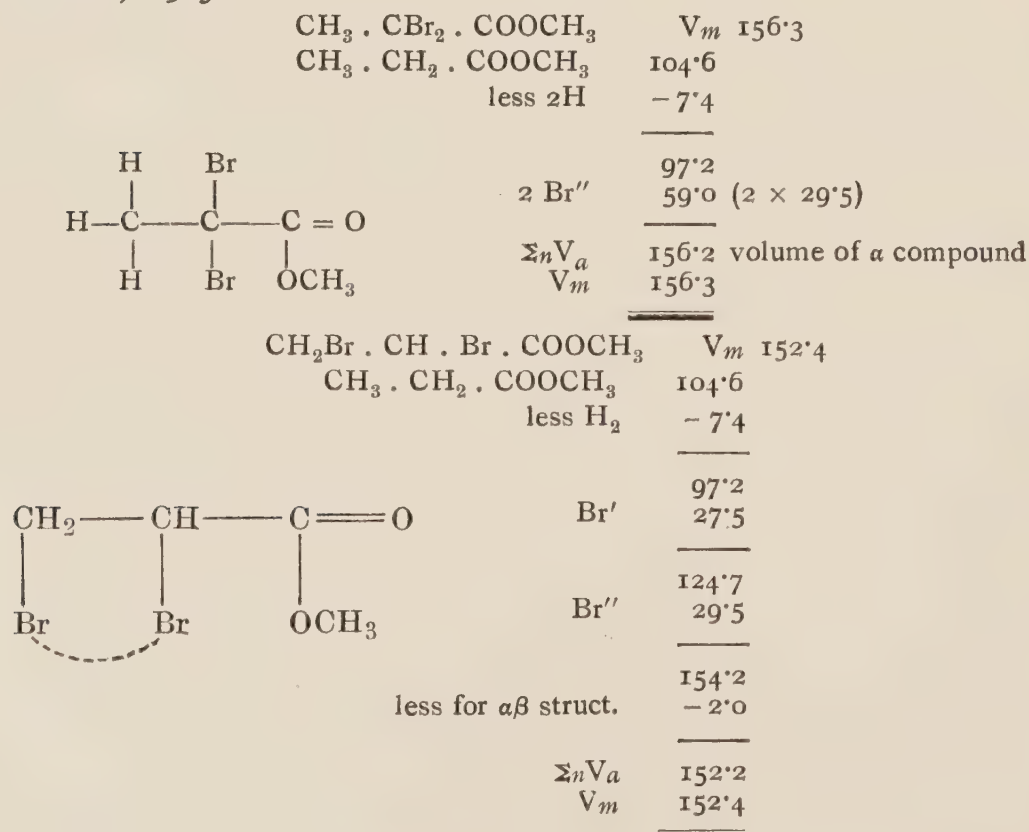
In order to facilitate the investigation we have calculated the volumes of the corresponding  $\alpha$  dibrom esters. For the  $\alpha\beta$  dibrom methyl compound  $C = 0.525$



There is thus a considerable contraction for the  $\alpha\beta$  compound as compared with the other.

Starting from methyl propionate we can calculate the result, remembering that the volume of an  $\alpha$  bromine atom (from acid group) is larger than one in the  $\beta$  position with reference to this group.

The  $\beta$  bromine atom which is at the end of a chain only possesses a volume of  $27.5$ , whilst one in the  $\alpha\beta$  has a larger volume,  $29.5$ .

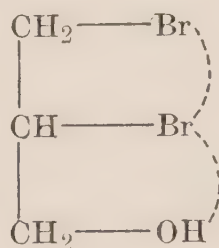




The contraction  $-3.9$ , already noticed, is made up as follows:—

$$\begin{array}{r}
 -2.0 \text{ for } \alpha\beta \text{ struct.} \\
 -2.0 \text{ for } \Delta \text{ between } \alpha \text{ and } \beta \text{ bromine} \\
 \hline
 \Delta \quad -4.0 \\
 \hline
 \end{array}$$

This may also be shown from an examination of dibrom propyl alcohol.



3CH <sub>2</sub>	66.3
Br'	27.5
Br''	29.5
O'	7.4
	<hr/>
	130.7
for $\alpha\beta$ struct.	-6.2
	<hr/>
$\Sigma_n V_a$	124.5
$V_m$	124.3
	<hr/>

$\alpha\beta$ dibrom	propionic methyl ester.	$V_m$ .	$\Delta$ .
	CH <sub>2</sub> Br . CHBr . COOCH <sub>3</sub>	152.3	
			26.3
	CH <sub>2</sub> Br . CHBr . COOC <sub>2</sub> H <sub>5</sub>	178.6	
			26.0
	CH <sub>2</sub> Br . CHBr . COOC <sub>3</sub> H <sub>7</sub>	204.6	

The  $\Delta$  for CH<sub>2</sub> is thus an unusually large number for compounds like the above. The only explanation is that there is an augmentation for complexity. Thus the equivalent volume in CH<sub>2</sub> units is  $\frac{178.6}{22.1} = 8$ . We have noticed that compounds of the order of complexity of octane (C<sub>8</sub>H<sub>18</sub>) are subject to augmentations for the above reason. Elsewhere the augmentation per CH<sub>2</sub> increase has been shown to be equal to  $+3.5$  in certain classes like the esters. Frequently the augmentation starts from the methyl ester.

$\alpha$ dibrom propionic ethyl ester		
$\text{CH}_3 \cdot \text{CBr}_2\text{COOC}_2\text{H}_5$		$V_m$ 181.7
$\alpha\beta$ $\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{COOC}_2\text{H}_5$		178.6
		<hr/>
		$\Delta$ - 3.1
		<hr/>
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$		127.7
less $2\text{H}$		- 7.4
		<hr/>
		120.3
$2\text{Br}''$		59.0 ( $2 \times 29.5$ )
		<hr/>
		179.3
augm. for complex.		+ 3.5 ( $1 \times 3.5$ )
		<hr/>
$\Sigma_n V_a$		182.8
$V_m$		181.7
		<hr/>
		<hr/>
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$		127.7
less $\text{H}_2$		- 7.4
		<hr/>
		120.3
$\text{Br}'$		27.5
		<hr/>
		147.8
$\text{Br}''$		29.5
		<hr/>
		177.3
less for $\alpha\beta$ struct.		- 2.0
		<hr/>
		175.3
augm. for complex.		+ 3.5 ( $1 \times 3.5$ )
		<hr/>
$\Sigma_n V_a$		178.8
$V_m$		178.6
		<hr/>
		<hr/>
$\text{CH}_2\text{Br} \cdot \text{CHBr} \cdot \text{COOC}_3\text{H}_7$		204.6
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOC}_3\text{H}_7$		149.9
less $\text{H}_2$		- 7.4
		<hr/>
		142.5
$\text{Br}' + \text{Br}''$		57.0
		<hr/>
		199.5
less for $\alpha\beta$ struct.		- 2.0
		<hr/>
		197.5
augm. for complex.		+ 7.0 ( $2 \times 3.5$ )
		<hr/>
$\Sigma_n V_a$		204.5
$V_m$		204.6
		<hr/>
		<hr/>

It is remarkable that neither the :O nor the  $\text{OCH}_3$  groups cause contractions.

## The Volume of :O in Union with S, N, and P.

It has been shown that the volume of :O in union with carbon varies from 7·4 to 11·0.

Its volume, when the atoms to which it is attached are N, S, P, is however different—uniformly so far as we can see

$$[:O] = 8\cdot2.$$

This is illustrated by a number of compounds which have been investigated by Thorpe, but since their full consideration demands a knowledge of the volumes of nitrogen, phosphorus, and sulphur, this is left till later. We content ourselves at present with one or two calculations which do not involve this knowledge.

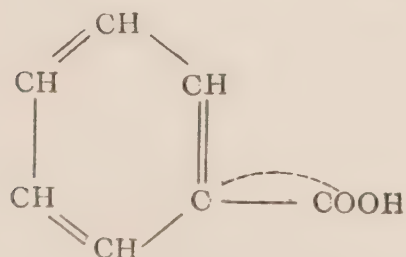
POCl <sub>3</sub>	101·4
PCl <sub>3</sub>	93·3
Δ for :O	8·1
<hr/>	
POBrCl <sub>2</sub>	107·4
PBrCl <sub>2</sub>	99·2
Δ for :O	8·2
<hr/>	
SO <sub>2</sub> Cl <sub>2</sub>	86·3
SOCl <sub>2</sub>	78·0
Δ for :O	8·3

These results are sufficient to show that the volume of :O in these compounds is 8·2. The other cases which involve a knowledge of the volumes of nitrogen, phosphorus, and sulphur give similar results.

The Aromatic Acids.<sup>51</sup>

When the radical C<sub>6</sub>H<sub>5</sub> replaces the aliphatic radical R, a large contraction occurs.

Benzoic acid.



V <sub>m</sub>	126·9
C <sub>6</sub> H <sub>5</sub>	92·8
COOH	34·1



V <sub>m</sub>	152·4
C <sub>5</sub> H <sub>11</sub>	114·1
COOH	38·3

$$\Delta = -4\cdot2.$$

Phenyl propionic acid and cinnamic acids.

$  \begin{array}{c}  \text{CH} \\  \diagup \quad \diagdown \\  \text{CH} \quad \text{CH} \\  \diagdown \quad \diagup \\  \text{CH} \quad \text{C} - \text{CH}_2 - \text{CH}_2 - \text{COOH} \\  \diagup \quad \diagdown \\  \text{CH}  \end{array}  $		$  \begin{array}{c}  \text{CH} \\  \diagup \quad \diagdown \\  \text{CH} \quad \text{CH} \\  \diagdown \quad \diagup \\  \text{CH} \quad \text{C} - \text{CH} = \text{CH} - \text{COOH} \\  \diagup \quad \diagdown \\  \text{CH}  \end{array}  $	
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2$	$V_m$	$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}$	$V_m$
	170.9		162.7
	135.6		127.5
	<hr/>		<hr/>
COOH	35.3	COOH	35.2
	<hr/>		<hr/>
$\Delta = -3.0$		$\Delta = -3.1$	

The volumes of the residues  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 : \text{CH}_2$  and  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}$  have been obtained as follows:—

Ethyl benzene.		Cinnamene (styrolene).	
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_3$		$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$	
$V_m$	139.3	$V_m$	131.2
less H	3.7	less H	3.7
	<hr/>		<hr/>
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2$	135.6	$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}$	127.5

The fact that the two values of COOH are similar, even though the saturated and unsaturated compounds are different in constitution, is sufficiently remarkable.

Styrolene is made up as follows:—

$\text{C}_6\text{H}_5$	92.8
$\text{CH} : \text{CH}_2$	40.7
	<hr/>
$\Sigma V_a$	133.5
less for unsat. and assoc. with $\text{C}_6\text{H}_5$	-2.3
	<hr/>
$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$	131.2
	<hr/>

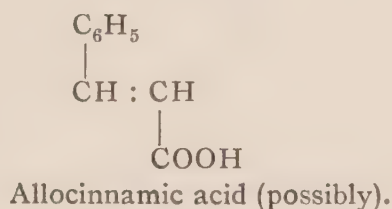
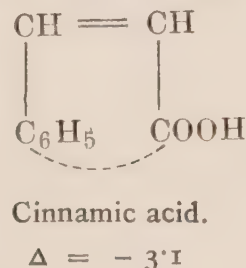
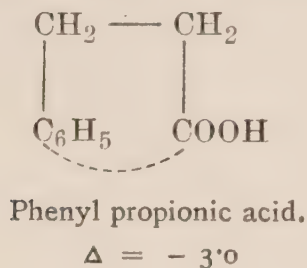
We thus work out the value for cinnamic acid

$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOH}$	
$\text{C}_6\text{H}_5$	92.8
$2\text{CH}$	37.0
COOH	38.3
	<hr/>
	168.1
less for unsat. and assoc. with $\text{C}_6\text{H}_5$ of hydrocarb. $\text{CH} : \text{CH}$	-2.3
	<hr/>
	165.8
less for assoc. of $\text{C}_6\text{H}_5$ and COOH	-3.1
	<hr/>
$\Sigma V_a$	162.7
$V_m$	162.7
	<hr/>



These numbers exactly agree. We are, however, met with the difficulty of the possibility of interaction between two unsaturated groups  $C_6H_5$  and  $COOH$ , when these groups are, on the basis of the ordinary formula, separated from one another.

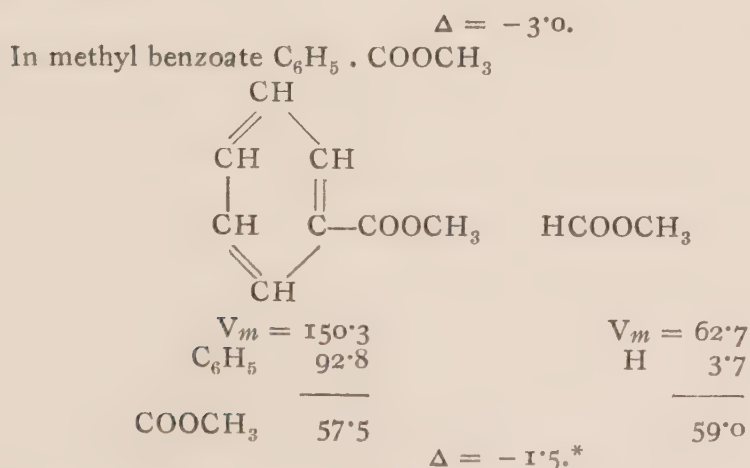
This difficulty can, however, be met by effecting a change in this formula, whereby the two groups are brought near each other. We may at the same time deal with phenyl propionic acid. The suggested formulæ for the two compounds are thus



These results thus agree with those obtained by ordinary chemical methods. There is a necessity for at least two modifications of cinnamic acid on the basis of the modified formulæ.

### Aromatic Esters.

It has been shown that in the aromatic acids the association of  $C_6H_5$  and  $COOH$  or other acid radical is responsible for a contraction



\* This difference may be in part explained by the fact that in methyl formate we have the combination  $H - C - OCH_3$ , in benzoic acid  $C - C - OCH_3$ . If we compare the latter with methyl acetate  $CH_3 - CO - OCH_3$  which has a similar grouping, we

Ethyl benzoate	$C_6H_5 \cdot COOC_2H_5$	$HCOOC_2H_5$	
$V_m$	174.2	$V_m$	84.6
$C_6H_5$	92.8	H	3.7
	<hr/>		<hr/>
$COOC_2H_5$	81.4		80.9
		$\Delta = -0.5.$	

We thus see that the association of  $C_6H_5$  and the following groups produce the contractions

	$\Delta$	
$C_6H_5 \left\{ \begin{array}{l} COOH \\ COOCH_3 \\ COOC_2H_5 \end{array} \right.$	$\begin{array}{l} -3.0 \\ -1.5 \\ -0.5 \end{array}$	$\begin{array}{c} O-C=O \\   \quad   \\ R \quad C_6H_5 \end{array}$

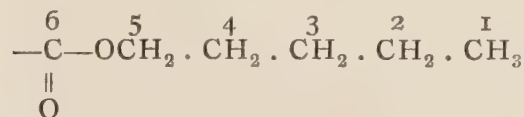
The effects just noticed depend

- (a) on the  $C_6H_5$  group ;
- (b) on the nature of the R group ;
- (c) possibly on the circumstance that the neighbouring carbons of the nucleus are unsaturated.

The group OH by itself occasions a contraction of only 0.8, so that the large contraction for benzoic acid must be due to the large amount of residual affinity connected with the group

Amyl benzoate	$C_6H_5 \cdot COOC_5H_{11}$	
	$C_6H_5$	92.8
	$CO_2$	33.3
	$C_5H_{11}$	114.1
	<hr/>	
		240.2
augm. for complex	$+7.0 (2 \times 3.5)$ for $C_6-C_4$	
	<hr/>	
$\Sigma_n V_a$	247.2	
$V_{mt}$	<u>247.3</u>	

The hydrocarbon chain of greater length than  $C_4$  occasions an expansion of + 3.5 for every  $CH_2$  added—

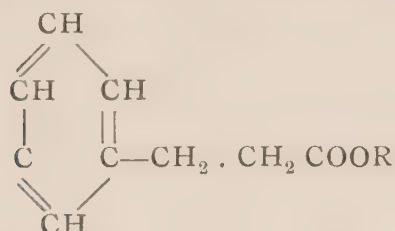


The volume of every member of this group of aromatic esters is thus easily calculated.

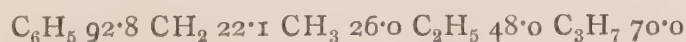
find for  $COOCH_3$ ,  $83.2 - 25.9 = 57.3$ , which is similar to that for the same group in benzoic acid. The volume of this group in ethyl benzoate  $C_6H_5 \cdot COOC_2H_5$  is about 1.5 higher than in methyl benzoate, as it should be

$$\cdot COOCH_3 = \cdot COOC_2H_5 - CH_2 = 81.4 - 22 = 59.4. \quad \Delta = +57.5 - 59.4 = -1.9.$$

## The Phenyl Propionic Esters.



In synthesizing the values of these compounds we utilize the general data:—



The augmentation for complexity above  $\text{C}_4$  at  $\Delta = + 3\cdot0$ .

Phenyl propionic propyl ester

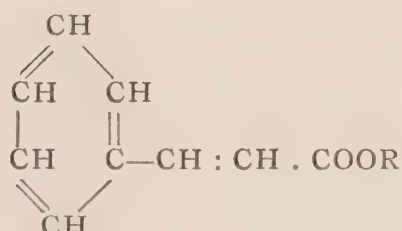


$\text{C}_6\text{H}_5$	92·8
$2\text{CH}_2$	44·2
$\text{CO}_2$	33·3
$\text{C}_3\text{H}_7$	70·0
	-----
	240·3
augm. ( $\text{C}_6 - \text{C}_4$ )	+ 6·0 ( $2 \times 3\cdot0$ )
	-----
$\Sigma_n V_a$	246·3
$V_m$	246·0
	=====

	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}_3$	195·2	196·3	- 1·1
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$	221·5	221·3	—
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOC}_3\text{H}_7$	246·0	246·3	—

The contraction - 1·1 in the case of the first compound agrees with former results.

## The Cinnamic Esters.



In these compounds the contraction seems to have disappeared, for on utilizing the following data:—



numbers similar to those obtained by experiment are calculated:—

## Cinnamic methyl esters

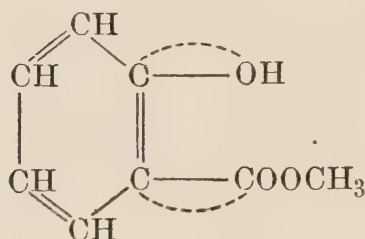
$C_6H_5 \cdot CH : CH \cdot COOCH_3$			
		$C_6H_5 \cdot CH : CH_2$	131.3
		less H	3.7
$C_6H_5$	92.8		
$2CH$	37.0		127.6
$COOCH_3$	59.0	$COOCH_3$	59.0
$\Sigma_n V_a$	188.8	$\Sigma_n V_a$	186.6
$V_m$	188.3	$V_m$	188.3
		$\Delta =$	+ 1.7*

There is thus an augmentation of 1.7 approximately equal to the effect for unsaturation.

Compound.	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$C_6H_5 \cdot CH : CH \cdot COOCH_3$	188.3	188.8	- 0.5
$C_6H_5 \cdot CH : CH \cdot COOC_2H_5$	213.75	213.7	—
$C_6H_5 \cdot CH : CH \cdot COOC_3H_7$	239.4	238.8	—

Methyl salicylate  $C_6H_4(OH)(COOCH_3)$ .

$V_m$  156.7.



$C_6H_4$	89.6
$COOCH_3$	59.0 in open-chain compounds.
$OH$	10.1 in alcohols.
	158.7
for assoc. of $OH$ and $C_6H_5$	- 0.8 (see for phenols)
	157.9
for assoc. of $COOCH_3$ and $C_6H_5$	- 1.5 (see for methyl benzoate)
	156.4
$\Sigma_n V_a$	156.4
$V_m$	156.7

\* Such an increase is noted in methyl ethyl and propyl acrylates when compared with the same salts of propionic acid :—

propionate	$\Delta$	acrylate
$OCH_3$ 104.6	5.9	98.7
$OC_2H_5$ 127.7	5.7	122.0
$OC_3H_7$ 151.0	5.8	145.2

$$\Delta = 7.2 - 5.8 = + 1.4$$

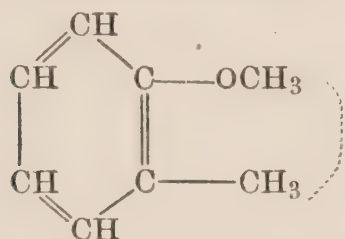


This is better seen from the following ;—

	$V_m$
$C_6H_5OH$	102.0
$C_6H_5 \cdot CO_2CH_3$	150.3
Sum	252.3
less for $C_6H_6$	-96.0
$\Sigma_n V_a$	156.3
$V_m$	156.7

The volume of methyl salicylate can thus be accounted for without supposing that there is any action between the two groups in the ortho-position. That the association of these two groups should normally interact is rendered probable by the following calculation :—

*o* Cresyl methyl ether.

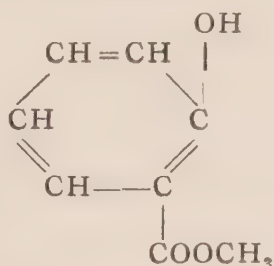


<i>p</i> cresyl methyl	148.0
<i>o</i> „ „	146.4
$\Delta$	= -1.6
by summation—	
$\Delta$	= -1.3

$C_6H_5OCH_3$	125.6
$C_6H_5 \cdot CH_3$	118.3
Sum	243.9
less $C_6H_6$	-96.0
$\Sigma_n V_a$	147.9
$V_m$	146.4
$\Delta$	+1.5 for <i>o</i> structure.

This compound is evidently “adjacent”.

The only explanation which we can offer is that methyl salicylate is an “opposed” compound.



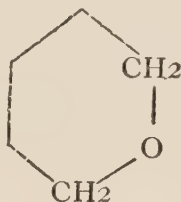
There is thus an “adjacent” modification also possible. A number of exceptions to the rule among the different compounds have been found, and since it is shown that their volumes do not involve any contraction although ortho compounds, we conclude that the groups are outside the range of each other's action. This

occurs under the circumstances that the groups are on opposite sides of the nucleus, that is the compounds are "opposed" compounds.

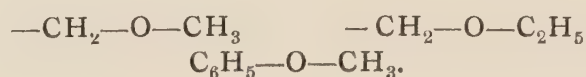
### The Volume of Ring Oxygen.<sup>52</sup>

A preliminary study of the subject might lead us to suppose that the volume of ring oxygen is invariable. A more minute examination of the data shows that this is not so.

In the first place ring oxygen

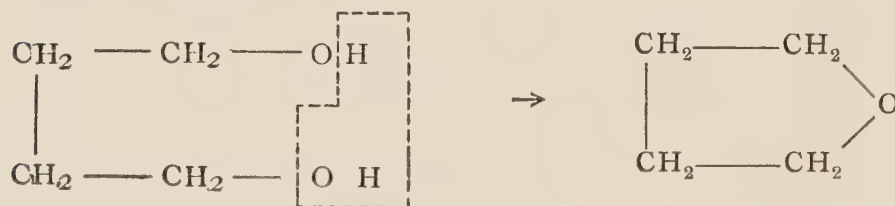


is apparently ethereal in character, and as such might vary, even as it does in



Moreover, in certain cases, it is found that ring oxygen, or indeed any other combination including oxygen, may be related to the volume which it possessed in the original compound.

If we consider such cases as

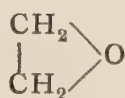


We see the possibility of  $\text{>O}$  retaining its volume relative to hydrogen in the ring compound.

A safe rule to follow is to assume the contraction compatible with the class of ring we are considering, and then finding the volume of oxygen by difference.

Ethylene oxide  $\text{C}_2\text{H}_4\text{O}$

$V_m$  50.0

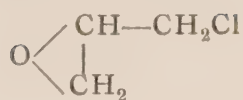


$\text{CH}_3\text{CHO}$  56.7  
 $2\text{CH}_2$  44.4

$\text{>O} = \underline{\underline{12.4}}$

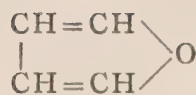
$2\text{CH}_2$	44.4
$> \text{O}$	12.4
	<hr/>
	56.8
less for $\square_3$ ring	-6.0
	<hr/>
$\Sigma_n V_a$	50.8
$V_m$	50.0
	<hr/> <hr/>

## Epichlorhydrin



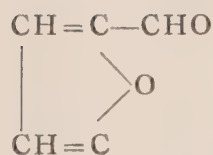
$\text{CH}_3-\text{O}-\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3$	$V_m$ 105.1
less $\text{C}_4\text{H}_{10}$	96.0
	<hr/>
$> \text{O} =$	<u>9.1</u>

$2\text{CH}_2$	44.2
$\text{CH}$	18.5
$\text{Cl}$	21.5
$> \text{O}$	9.1
	<hr/>
	93.3
less for $\square_3$ ring	-6.0
	<hr/>
$\Sigma_n V_a$	87.3
$V_m$	87.3
	<hr/> <hr/>

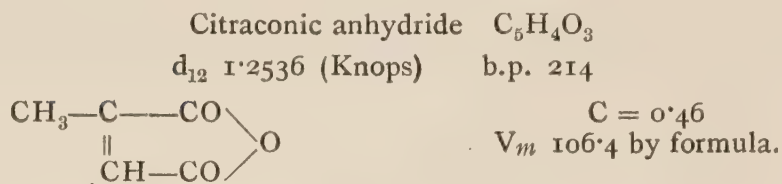
Furfurane  $\text{C}_4\text{H}_8\text{O}$  $V_m$  73.2

$\text{CH}_3 \cdot \text{CH}_2-\text{O}-\text{CH}_2 \cdot \text{CH}_3$	$V_m$ 106.3
less $\text{C}_4\text{H}_{10}$	96.0
	<hr/>
$> \text{O}$	<u>10.3</u>

$4\text{CH}$	74.0
$> \text{O}$	10.3
	<hr/>
	84.3
less for $\square_5$ ring	-11.0
	<hr/>
$\Sigma_n V_a$	73.3
$V_m$	73.2
	<hr/> <hr/>

Furfural  $\text{C}_5\text{H}_4\text{O}_2$  $V_m$  95.7.

$4\text{CH}$	74.0
$> \text{O}$	10.3
$\text{CO}$	22.1
	<hr/>
	106.4
less for $\square_5$ ring	-11.0
	<hr/>
$\Sigma_n V_a$	95.4
$V_m$	<u>95.7</u>

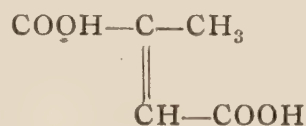
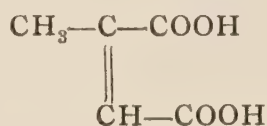


This compound is a derivative of methyl succinic acid and thus we might expect the volume of  $>O$  to be  $7.4$ .

$\text{CH}_2$	22.1
$2\text{CH}$	37.0
$2\text{CO}''$	52.0
$>O$	7.4
	<hr/>
	118.5
less for $\square_5$ ring	-11.0
	<hr/>
$\Sigma_n V_a$	107.5
$V_m$	106.4
	<hr/>

There is probably a contraction for the attachment of the group  $\text{CH}_3$  to an unsaturated system.

Citraconic and mesaconic acids



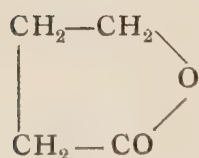
probably both possess similar volumes owing to the fact that there are two groups in apposition in the two compounds. The theoretical volumes are—

Citraconic anhydride	106.4
$\text{H}_2\text{O}$	14.8
	<hr/>
	121.2
less for $\alpha\beta$ struct.	-1.5
	<hr/>
$\Sigma_n V_a$	119.7
	<hr/>

The whole contraction is  $-3.1$ , but seeing that there is an expansion of  $+1.5$  for the ethenoid link, the resultant contraction is only  $-1.5$

Butyrolactone  $C_4H_6O_2$

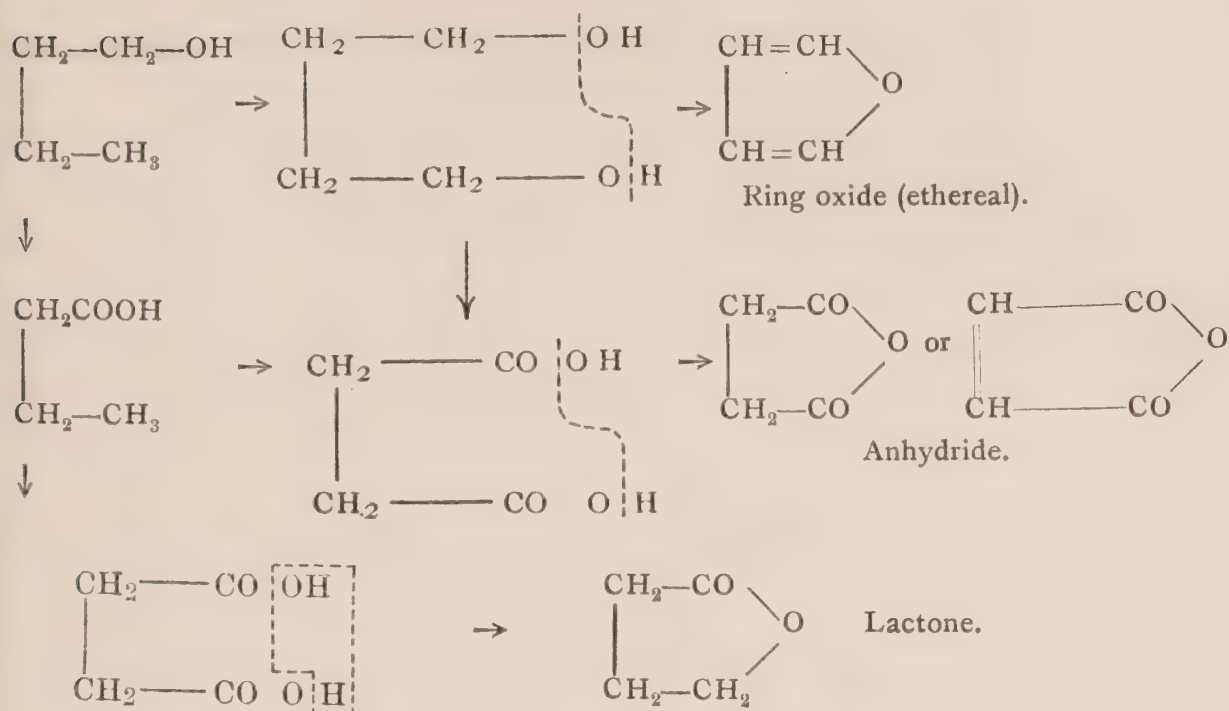
$d_0 \ 1.441$  (Saytzeff)      b.p.  $206$   
 $C = 0.46$        $V_m \ 90.0$  (by form.)



$3\text{CH}_2$	66.3
$\text{CO}''$	26.0
$>O$	9.6
	<hr/>
	101.9
less for $\square_5$ ring	-11.0
	<hr/>
$\Sigma_n V_a$	90.9
$V_m$	90.0
	<hr/>

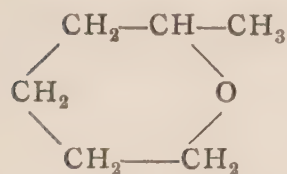
We have thus the following interesting series of compounds:—





In every case the different peculiarities of structure can be stated in terms of volume.

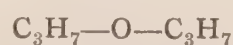
δ Hexylene oxide  $\text{C}_6\text{H}_{12}\text{O}$



$d_0$  0.8739

b.p. 104.0  $C = 0.46$

$V_m$  129.2 by formula.



$V_m$  127.9  
 $\text{C}_5\text{H}_{12}$  117.8

$V_m$  151.3  
 $\text{C}_6\text{H}_{14}$  139.9

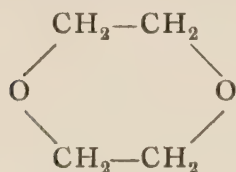
$> \text{O}$  10.1

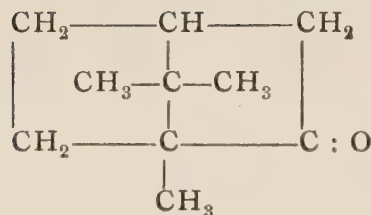
$> \text{O}$  11.4

$6\text{CH}_2$  132.6  
 $> \text{O}$  11.4

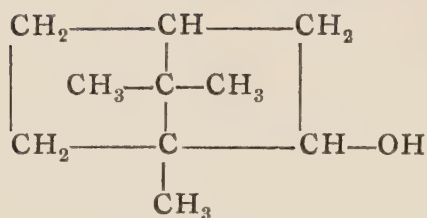
less for  $\square_6$  ring 144.0  
- 15.0

$\Sigma_n V_a$  129.0  
 $V_m$  129.2

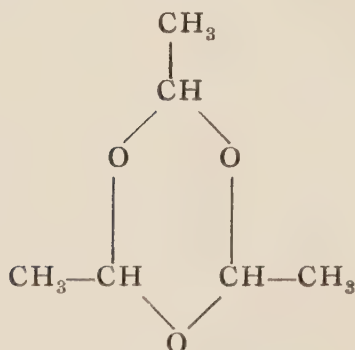
Diethylene dioxide  $C_4H_8O_2$  $d_0$  1.0482      b.p. 102.0 $C = 0.46$        $V_m$  94.7
$$\begin{array}{r} 4CH_2 \\ 2 > O \end{array} \quad \begin{array}{r} 88.4 \\ 21.0 \text{ average } 10.5 \end{array}$$
less for  $\square_6$  ring  $\begin{array}{r} 109.4 \\ -15.0 \end{array}$ 

$$\begin{array}{r} \Sigma_n V_a \\ V_m \end{array} \quad \begin{array}{r} 94.4 \\ 94.7 \end{array}$$
Camphor  $C_{10}H_{16}O$  $V_m$  187.6

$$\begin{array}{r} C_{10}H_{16} \\ : O \end{array} \quad \begin{array}{r} 207.2 \\ 11.0 \end{array}$$
less for ring  $\begin{array}{r} 218.2 \\ -30.6 \end{array}$ 

$$\begin{array}{r} \Sigma_n V_a \\ V_m \end{array} \quad \begin{array}{r} 187.6 \\ 187.6 \end{array}$$
Borneol  $C_{10}H_{18}O$  $V_m$  190.5

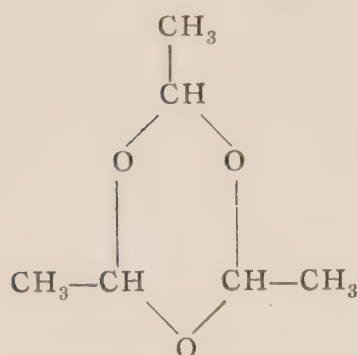
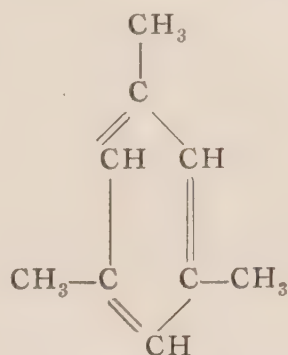
$$\begin{array}{r} C_{10}H_{18} \\ O \end{array} \quad \begin{array}{r} 214.6 \\ 6.4 \text{ (as in alcohols)} \end{array}$$
less for ring  $\begin{array}{r} 221.0 \\ -30.6 \end{array}$ 

$$\begin{array}{r} \Sigma_n V_a \\ V_m \end{array} \quad \begin{array}{r} 190.4 \\ 190.5 \end{array}$$
Paraldehyde  $C_6H_{12}O_3$  $V_m$  151.0 (Schiff).

$$\begin{array}{r} C_6H_{12} \\ 3 > O \end{array} \quad \begin{array}{r} 133.2 \\ 33.0 \end{array}$$
less for  $\square_6$  ring  $\begin{array}{r} 166.2 \\ -15.0 \end{array}$ 

$$\begin{array}{r} \Sigma_n V_a \\ V_m \end{array} \quad \begin{array}{r} 151.2 \\ 151.0 \end{array}$$

Paraldehyde has a similar structure to that of mesitylene.

Paraldehyde  $\text{C}_6\text{H}_{12}\text{O}_3$  $V_m$  151.0Mesitylene  $\text{C}_6\text{H}_2\text{C}_3$ 

162.4

$$\Delta = -11.4$$

The difference in volume should be on the assumption of similarity of structure.

$$\begin{aligned}
 \Delta &= 3\text{C} - 3\text{O} = 3(\text{C} - \text{O}) = 3(14.8 - 11.0) \\
 &= 3 \times 3.8 = 11.4
 \end{aligned}$$

This difference is identical with the one observed.

### Summary of Chapter on Oxygen.

Oxygen has been shown to possess quite a number of values, according to its position and function. This is in opposition to Kopp's idea that only two values are found:—

$$\text{O}' = 7.8 \quad \text{O}'' = 12.0$$

The reason doubtless is, that the volume of O and every other atom varies somewhat according to its environment. Besides this, we ought to consider the nature of the forces acting, that is the residual affinity. An exact notion of these circumstances eludes us. All we can do is to tabulate the values, and compare them with the known constitutions of the compounds. Under favourable circumstances we can draw up a series of rules which may act as guides in enabling us to decide on the real volume of oxygen in an uninvestigated compound. The inquiry has not gone quite far enough to do this with precision. In molecular volumes we roughly classify the varying types of oxygen as:—

(a) Hydroxyl oxygen	$\text{O}'$	5.6 – 7.4
(b) Etheral oxygen	$>\text{O}$	9.0 – 11.0
(c) Aldehydic and ketonic	$\text{O}''$	7.4 – 11.0
(d) Carboxylic	$\text{O}_2$	16.4 – 18.0

TABLE LXX.—VALUES OF OXYGEN IN ORGANIC COMPOUNDS.

	Aliphatic.	Aromatic, etc.
O'	6.4 (in alcohols)	5.6 (in phenols)
	7.4 (in esters) or [11.0]*	7.4 (in esters) or [11.0]*
	9.5 (in —OCH <sub>3</sub> )	7.5 (in —OCH <sub>3</sub> )
>O (ethereal)	10.11 (in —OR)	10.11 (in —OR)
O''		
aldehydic and	7.4 (aldehydes)	
ketonic	11.0 (ketones)	
O''		
carboxylic	11.0 (in acids and esters) or [7.4]*	
O''		
in union with	8.3	
S, P, N		

*Ring oxygen as in ethers.*

A requirement of the first importance is to know how the volume of oxygen varies according to its position in a chain. In some cases the information is definite and complete, in others it is very indecisive.

	H—O—R	CH <sub>3</sub> —O—R	C <sub>2</sub> H <sub>5</sub> —O—R	C <sub>4</sub> H <sub>9</sub> —O—R
V <sub>a</sub>	6.4	9.6	10	11

These facts show that the volume of the terminal oxygen is always the minimum value, and the volume increases as the oxygen passes into the interior of the molecule.

Similar results are shown in the following:—

CH <sub>3</sub> —O—C—R    O	C <sub>2</sub> H <sub>5</sub> —O—C—R    O	C <sub>3</sub> H <sub>7</sub> —O—C—R    O
30.6	32.0	32.7

When the CO<sub>2</sub> is in the middle of the chain the volume is a maximum. Another way of stating the same thing is to suppose that the groups CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub> produce depressing actions on the volume in an order which is in the inverse of the order in which they are written down.

CH <sub>3</sub> . CH <sub>2</sub> . COOCH <sub>3</sub>	V <sub>m</sub> 104.6	Σ <sub>n</sub> V <sub>a</sub> 107.0	Δ -2.4
CH <sub>3</sub> . CH <sub>2</sub> . COOC <sub>2</sub> H <sub>5</sub>	127.7	129.1	-1.4
CH <sub>3</sub> . CH <sub>2</sub> . COOC <sub>3</sub> H <sub>7</sub>	151.0	151.2	—

That the methyl group is specially concerned in producing a contraction is shown by the following—

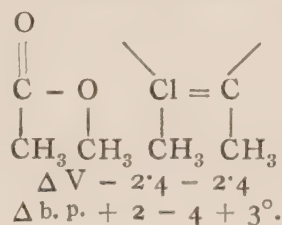
CH <sub>3</sub> . COOCH <sub>3</sub>	V <sub>m</sub> 83.2	Σ <sub>n</sub> V <sub>a</sub> 85.3	-2.1
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Similarly in aromatic compounds there are contractions when

\* See Note on page 176.



two  $\text{CH}_3$  groups are in the ortho position relative to each other. By analogy we have the configurations :—



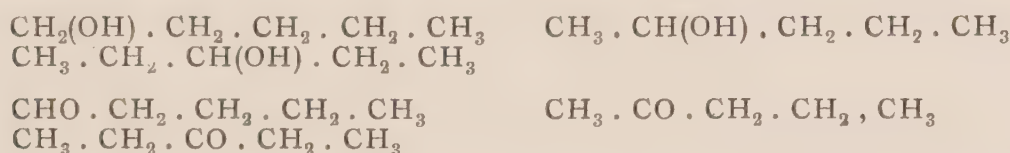
An examination will show that the boiling-points of the methyl esters are always 2-4 degrees higher than what might be expected from the differences.

For some reason the acids show an augmentation instead of a depression, which fact is contrary to expectation.

Acid.	$V_m$ .	$\Delta$ .	Ester.	$V_m$ .
$\text{CH}_3 \cdot \text{COOH}$	63.9	+ 1.2	$\text{HCOOCH}_3$	62.7
$\text{C}_2\text{H}_5 \cdot \text{COOH}$	88.4	+ 3.8	$\text{H} \cdot \text{COOC}_2\text{H}_5$	84.6
$\text{C}_3\text{H}_7 \cdot \text{COOH}$	107.9	+ 1.7	$\text{H} \cdot \text{COOC}_3\text{H}_7$	106.2
$\text{C}_4\text{H}_9 \cdot \text{COOH}$	130.0	+ 2.4	$\text{HCOOC}_4\text{H}_9$	127.6
$\text{C}_5\text{H}_9 \cdot \text{COOH}$	152.9	+ 2.4	$\text{HCOOC}_5\text{H}_{11}$	150.5

The reason for this is not known.

We may also consider the question of the change in volume under the following circumstances :—



The information on these matters is meagre and inconclusive.

A general rule seems to be that the volume of a typical atom increases as it is placed further from the end of the chain, and attains its maximum when it is attached to the central carbon atom. Accompanying this is a corresponding depression in the boiling-point of the compound.

As a result of careful examination we think it desirable to exclude such general and vague ideas as symmetry, shape, etc., as possible influences operative in deciding the volume of a compound, and to substitute more precise notions, as the specific actions or influences, due to particular groups. The forces acting are doubtless those of residual affinity, and though symmetry, etc., are involved, yet it is only indirectly.

The most probable explanation of the facts, and one which is intimately concerned with the question of what we mean by molecular volumes, is as follows: As a result of residual affinity

arising from the molecule, there is produced an external field of strength which may be the sum total of the effects arising from individual atoms. This external field causes an intermolecular pressure which at once influences the boiling-point and the molecular volumes. If the field is relatively great, the boiling-point is raised and the volume diminished by compression and vice versa.

Thus (*a*) the alcohols are more *reactive* than the ethers. We find relatively high boiling-points and small volumes. The effect of an oxygen atom diminishes as it tends towards the middle of the chain.

(*b*) Similarly when we compare *aa* with *aβ* compounds we are comparing the effect of the combinations—CH<sub>2</sub>—CHX<sub>2</sub> and —CHX—CH<sub>2</sub>X. As X becomes removed from the end of the chain the boiling-point diminishes and the volume increases. The two atoms X, however, may also influence one another, and by their proximity when attached to different carbon atoms intensify each other's action, and thus the external field. This would account for the observed increase in boiling-point and diminished volume as compared with *aa'* compounds.

(*c*) The above considerations also affect ortho compounds as compared with para, and from what we have seen the methyl esters as compared with ethyl and propyl.

We should expect to find the capillary constants and viscosity coefficients of the high boiling-point compounds relatively high. This is what we do find.

#### NOTE.

##### Alternative Interpretation of $\Sigma V_a \cdot (O_2) = 18.5$ .

*It has been shown that O<sub>2</sub> in the esters possesses a volume*

$$\begin{array}{l} O_2 = 18.5, \\ \text{and } O'' = 11.0, \qquad O' = 7.4 \text{ (see p. 147),} \end{array}$$

*which numbers are similar to those indicated by Kopp.*

*Whilst this book was passing through the press an alternative explanation of the value of O<sub>2</sub> suggested itself, and it has much to recommend it. The chief advantage is that thereby a considerably greater consistency in theory is secured than by the former explanation.*

Thus:—

$O'' = 7.4$  (as in the aldehydes and ketones and doubly bound oxygen generally).

$O'$



$O' = 9.1$  (in methyl esters);       $9.9$  (methyl ethers).  
        $= 11.0$  (in higher esters);       $11.0$  (higher ethers).  
        $= 12.0$  (in acids).

The value of  $O'$  is similar to that of ethereal oxygen, which from a chemical point of view it is. The only difficulty is to account for the value  $O'' = 11$  in  $\text{COCl}_2$  and analogous compounds.

If the above be the true explanation, which we believe it is, Kopp's theory,  $O'' = 12$ ,  $O' = 7.8$ , is found to be once again at fault.

## CHAPTER V.

### THE MOLECULAR VOLUMES OF SULPHUR COMPOUNDS.

#### The Element Sulphur.

THE molecular volume of sulphur in the uncombined state is

$$S = 21.8 \quad \text{Ramsay}^{52}$$

and in the combined state

$$\begin{aligned} S_1 &= 21.6 \\ S_2 &= 25.6 \end{aligned}$$

The first value in the combined state is for doubly bound sulphur : S.

The second value is considered to be the normal one.

In considering the characteristics of sulphur at, and near the boiling-point, we find—

fusion-point	111.5	yellow mobile liquid
„	250.0	dark and thick
„	300.0	dark but thin
boiling-point	440.0	orange-coloured vapour.

In the liquid state,

the molecules are probably  $S_{10}$  and  $S_8$ .

At any rate in the vapour, the complexity is

$$\begin{array}{ll} \text{at } 500^\circ & S_6. \\ \text{and at } 1000^\circ & S_2 \end{array}$$

There is thus dissociation



The formula for  $S_2$  is certainly



but the molecule  $S_6$ , so far as we know, has not been explained.

The formula for  $S_6$  must explain at least three facts—

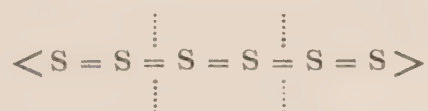
- (a) The existence of colour.
- (b) The easy decomposability of  $S_6$  into  $3S_2$ .
- (c) An average value of sulphur of 21.8.



The colour phenomenon can be explained on the assumption that the formula for  $S_6$  contains at least three double bonds.

The average value for sulphur of 21.8 can be explained either by an open-chain formula or by one which, as a whole or in part, involves ring structure.

The open chain formula would be



This explains colour and easy decomposability.

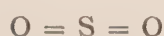
The possibility of this type of formula depends on whether sulphur has sufficient power of self combination to form a molecule with this length of chain.

That this may be so is suggested by a formula for potassium pentasulphide



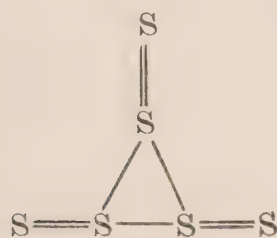
We must also assume that  $= S =$  possesses the volume of 21.8, if we take and consider the above formula.

The volume of sulphur in



25.6 is contrary to this idea.

Possible ring formulæ are—

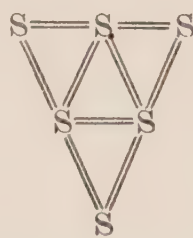


22.5



Average volumes.

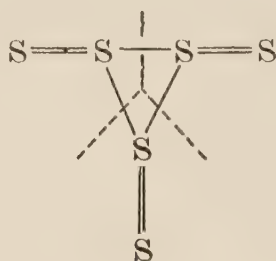
22.7



21.6

The only one which gives an average volume similar to the experimental one is the third, but should be excluded owing to the fact that easy decomposition is not suggested.

In spite of the fact that the value of  $S$  for the first, is slightly higher than that indicated by experiment, it seems the most satisfactory one. It explains the phenomena of colour and easy decomposability.



The average volume of sulphur is calculated thus—

3 atoms of : S	$3 \times 25.6$	76.8
3 „ S	$3 \times 21.6$	64.8
		<hr/>
6 atoms of S		141.6
less for ring		-6.5
		<hr/>
S <sub>6</sub>		135.1
S		22.5

Probably we do not know all the facts connected with a formula of the above type. It is quite possible that there are influences which would tend to lower the average value to the one given by experiment.

### The Halogen Derivatives of Sulphur (Thorpe, loc. cit.).

Sulphur di-chloride.



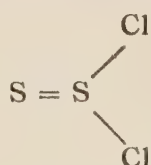
b.p. 64	d <sub>0</sub> 1.62	C 0.46
V <sub>m</sub>	68.8 (by formula)	
S	25.6	
2Cl	43.2	
		<hr/>
Σ <sub>n</sub> V <sub>a</sub>	68.8	
V <sub>m</sub>	68.8	
		<hr/>

Sulphur monochloride.

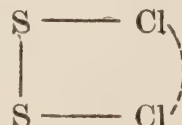



V<sub>m</sub> 90.3 (Thorpe).

Two formulæ are possible—



and



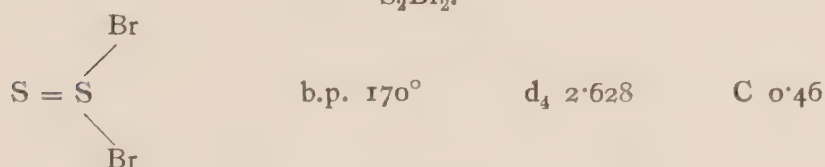
The first is the analogue of  $\text{O}=\text{S}$  , and the second is an

*αβ* compound.

1st formula.		2nd formula.	
$\begin{array}{c} \diagup \\ = \text{S} \\ \diagdown \end{array}$	25.6	$\begin{array}{c} 2\text{S} \\ 2\text{Cl} \end{array}$	$\begin{array}{c} 51.2 \ (2 \times 25.6) \\ 43.2 \ (2 \times 21.6) \end{array}$
$\begin{array}{c} = \text{S} \\ 2\text{Cl} \end{array}$	$\begin{array}{c} 21.6 \\ 43.2 \end{array}$		$\begin{array}{c} 94.4 \\ - 3.1 \end{array}$
		less for $\alpha\beta$ str.	
$\Sigma_n V_a$	90.4	$\Sigma_n V_a$	91.3
$V_m$	<u>90.3</u>	$V_m$	<u>90.3</u>
		$\Delta$	<u>- 1.0</u>

The validity of the first is suggested by the calculations.  
One other compound like the above is

Sulphur monobromide.



	$V_m \ 100.0$
$\begin{array}{c} \diagup \\ = \text{S} \\ \diagdown \end{array}$	25.6
$\begin{array}{c} = \text{S} \\ 2\text{Br} \end{array}$	$\begin{array}{c} 21.6 \\ 54.0 \ (2 \times 27.0) \end{array}$
$\Sigma_n V_a$	101.2
$V_m$	<u>100.0</u>

The calculations are found to be distinctly in favour of the first formula, to which we adhere.

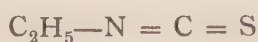
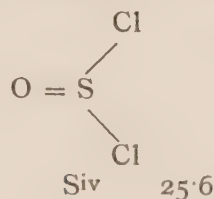
We possess also the following evidence for the atomic values which have been proposed:—

$\text{SCl}_2$	68.8
$\text{SSCl}_2$	<u>90.3</u>
$: \text{S}$	<u>21.5</u>

It follows that  $\begin{array}{c} \diagup \\ = \text{S} \\ \diagdown \end{array}$  possesses a volume of 25.6

and  $\begin{array}{c} = \text{S} \\ 2\text{Cl} \end{array}$  one of 21.6

This is proved by the following results:—



	$V_m$	99.3
$\text{C}_2\text{H}_5 \cdot \text{N} : \text{C}$	$>$	<u>77.5</u>
$: \text{S}$		<u>21.8</u>

Thorpe has come to the same conclusion, but in a different way. Thus:—

SSCl <sub>2</sub>	V <sub>m</sub> 90.3
Cl <sub>2</sub>	45.4 (2 × 22.7)
2S	45.0 (2 × 22.5)
Σ <sub>n</sub> V <sub>a</sub>	90.4
V <sub>m</sub>	90.3

We have seen that the two sulphur atoms are not equal in value, but possess respectively the two volumes characteristic of this element. Moreover, we have reason to think that the chlorine atoms do not possess quite so large a volume as Thorpe and, indeed, Kopp supposed.

Thorpe has investigated a number of compounds which are similar to the above, but containing oxygen, and the present theory affords valuable evidence as to their structure. The conclusions arrived at more than thirty years ago (1881) are considered to be invalid. They were obtained by means of Kopp's numbers. The latter thought that only two values for oxygen are met with,

$$O' \ 7.8 \text{ and } O'' \ 12.0.$$

This is not the case. At any rate, the particular solution of the problem arrived at here hinges on the volume of oxygen.

SCl <sub>2</sub>	68.8	SOCl <sub>2</sub>	78.0
SOCl <sub>2</sub>	78.0	SO <sub>2</sub> Cl <sub>2</sub>	86.3
O''	9.2	O''	8.3

Similar volumes are found when oxygen is united to phosphorus and nitrogen.

PCl <sub>3</sub>	93.3	NO <sub>2</sub>	32.0	N	15.6
POCl <sub>3</sub>	101.4			20	16.6
O''	8.1	—N=O		Σ <sub>n</sub> V <sub>a</sub>	32.2
				V <sub>m</sub>	32.0

The volume of oxygen in thionyl chloride is apparently slightly larger than the other value. This is also the case for one of the oxygens in sulphuryl chloride and other compounds. The reason for this is not very apparent, but it at least explains the volume of sulphur dioxide SO<sub>2</sub>.



$$\begin{array}{rcl}
 \text{SO}_2 & \text{O} = \text{S} = \text{O} & \\
 V_m & 43\cdot9 & \\
 = \text{S} = & 25\cdot6 & \\
 2\text{O}'' & 18\cdot4 \quad (2 \times 9\cdot2) & \\
 \hline
 \Sigma V_a & 44\cdot0 & \\
 V_m & 43\cdot9 & \\
 \hline
 \hline
 \end{array}$$

If this be so, then the volume for chlorine is 21·6.

$$\begin{array}{rcl}
 \text{SO}_2\text{Cl}_2 & 68\cdot8 & 2\text{Cl} = 68\cdot8 - 25\cdot6 = 43\cdot2. \\
 & & \text{Cl} \quad 21\cdot6.
 \end{array}$$

This conclusion may be arrived at in another way—

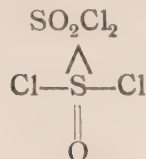
$$\begin{array}{rcl}
 \text{SO}_2\text{Cl(OH)} & 75\cdot05 & \\
 \text{SO}_2\text{Cl} = 75 - 10\cdot4 = 64\cdot6 & (\text{OH} = 6\cdot7 + 3\cdot7) & \\
 \text{SO}_2\text{Cl}_2 & 86\cdot3 & \\
 \text{SO}_2\text{Cl} & 64\cdot6 & \\
 \hline
 \text{Cl} & 21\cdot7 & \\
 \hline
 \hline
 \end{array}$$

Thus—

$$\text{S} = 25\cdot6 \quad \text{O}'' = 9\cdot1 \text{ and } 8\cdot3 \quad \text{Cl} = 21\cdot6$$

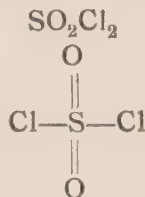
Utilizing these values, we find—

Thionyl chloride.



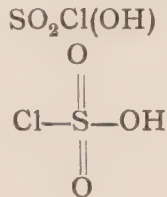
$$\begin{array}{rcl}
 \Sigma V_a & 78\cdot0 & \\
 V_m & 78\cdot0 &
 \end{array}$$

Sulphuryl chloride.



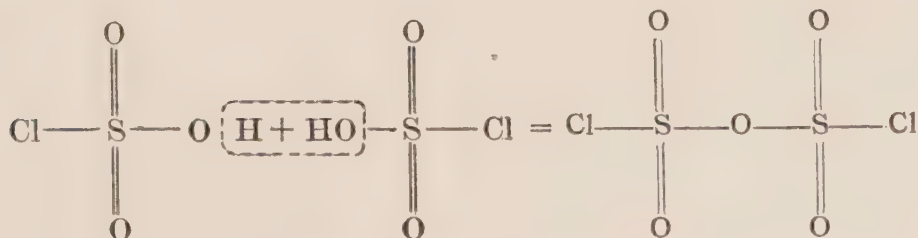
$$\begin{array}{rcl}
 & 86\cdot3 & \\
 & 86\cdot3 &
 \end{array}$$

Sulphuryl chlorhydrate.



$$\begin{array}{rcl}
 & 75\cdot1 & \\
 & 75\cdot0 &
 \end{array}$$

The latter compound by condensation gives disulphuryl chloride



$$\begin{array}{rcl}
 - \text{ClSO}_2 & = \text{ClSO}_2\text{OH}-\text{OH} & \\
 & = 75\cdot0 - 10\cdot4 = 64\cdot6. &
 \end{array}$$

The volume of —O— is thus—

$$\begin{array}{rcl}
 \text{Volume of ClSO}_2-\text{O}-\text{O}_2\text{SCl} & 133\cdot5 & \\
 2\text{ClSO}_2- & 129\cdot2 & \\
 \hline
 -\text{O}- & 4\cdot3 & \\
 \hline
 \hline
 \end{array}$$

This is a small value for oxygen, indeed, the smallest value known.

A possible explanation of this lies in the fact that in the aromatic hydroxy compounds like phenol  $C_6H_5OH$ , where OH is united to the nucleus  $C_6H_5-$ , there is a contraction of  $-1.4$ .

E.g. if $C_6H_5OH$ possess the volume	102.0
and $C_6H_6$ „ „	96.0
then O'	<u>6.0</u>

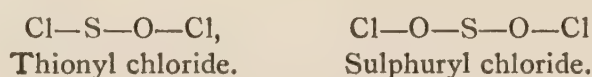
Since  $O' = 7.4$   $\Delta$  is  $6.0 - 7.4 = -1.4$ .

Now the  $-O-$  atom in disulphuryl chloride is joined on to two acid groups  $-SO_2Cl$ , or, at any rate, to groups possessing residual affinity. If we deduct  $2 \times 1.4$  from the normal value for this kind of oxygen we obtain the volume

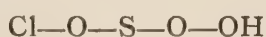
$$O = 7.4 - 2.8 = 4.6.$$

This number is not very different from that found, 4.3, and thus its remarkably small volume may possibly be explained.

The formulæ supported by the molecular volume theory, and which are considered to possess doubly bound oxygen, are different to those which Thorpe has proposed, based on the conclusion that the oxygen atom is of the hydroxyl type. Such formulæ would be



In addition to the fact that the atomic volume of oxygen found, in spite of its similarity to the value for one similar to  $-O-$ , is a doubly bound one, a formula of this type could hardly apply to sulphuryl chlorhydrate, for



is extremely improbable.

The formulæ which have been proposed are also more in accord with the properties of the compounds and their genetic relationships. It should also be observed that they support the view that sulphur is tetra and hexavalent in the compounds rather than divalent.

### The Sulphur Oxides, Acids, and Ethereal Salts of the Acids.

These oxides are two in number,  $SO_2$  and  $SO_3$ .

Sulphur dioxide.

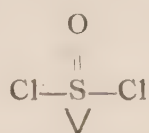


$V_m$  43.9.

Oxygen appears to have the volume 9·2 in this compound

S	25·6
2O	18·4
$\Sigma nV_a$	44·0
$V_m$	43·9

This is also seen in thionyl chloride.



$V_m$	78·0
$V_{m\text{SCl}_2}$	68·8
: O	9·2

Sulphur trioxide.

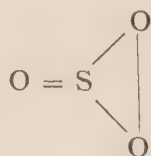


This compound possesses a molecular volume but little different from that for  $\text{SO}_2$ . There must consequently be a considerable contraction.

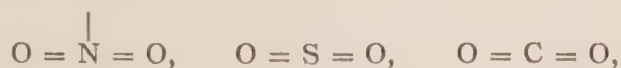
$V_m$	44·3
S	25·6
3O	24·9
$\Sigma nV_a$	50·5
$V_m$	44·3
$\Delta$	-6·2

This contraction is evidently connected with the presence of a three-membered single ring.

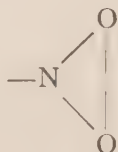
The formula to be accorded to this compound is for this reason considered to be represented by



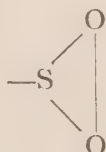
so that sulphur is tetravalent instead of hexavalent. It is remarkable that none of the groups  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{CO}_2$  contain this ring. The formulæ are



and not



,



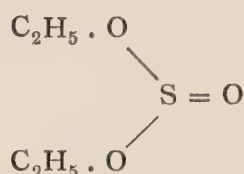
,



## Sulphurous ethyl ether.

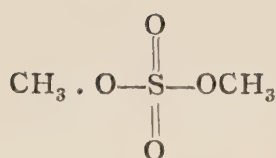
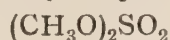


b.p. 161°

 $d_0$  1.106C 0.50 as in  $(C_2H_5O)CO$  $V_m$  146.5 (by formula).

$C_4H_{10}$	96.0
S	25.6
3O	24.9
<hr/>	
$\Sigma nV_a$	146.5
$V_m$	146.5
<hr/>	

## Methyl sulphate.



b.p. 188°

 $d_{15}$  1.333

C . 0.50.

 $V_m$  112.2 by formula.

$2CH_3$	52.0
$SO_2$	42.2
$O_2$	18.6
<hr/>	

$\Sigma nV_a$	111.8
$V_m$	112.2
<hr/>	

## Ethyl sulphate.



b.p. 208°

 $d_{19}$  1.1837 $V_m$  155.7 $\Sigma nV_a$  156.8

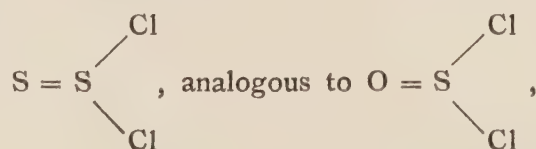
## Doubly Bound Sulphur.

Sulphur, as already indicated, has two values. The second has just been found to be associated with the ring compounds thiophene and methyl pent thiophene. It is also found in the thiocarbimides and thiocyanates.

Compound.	$V_m$ .	S.	$V_m$ .	The Cyanides.
$CH_3 \cdot S \cdot CN$	78.2	21.9	56.3	$CH_3 \cdot CN$
$C_2H_5 \cdot S \cdot CN$	100.1	21.8	78.3	$C_2H_5 \cdot C \cdot N$
$C_6H_5 \cdot S \cdot CN$	143.4	21.8	121.6	$C_6H_5 \cdot CN$

A similar number is found to be connected with doubly bound sulphur.

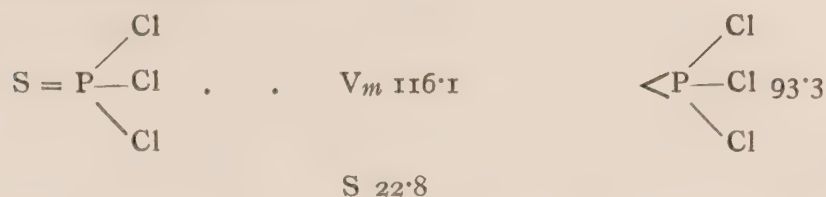
If sulphur mono-chloride possess the formula



the volume of : S would be 21.8 (q.v.) whilst that of  $= S \begin{array}{l} \diagup \\ \diagdown \end{array}$  would be 25.6,



Phosphorus sulpho chloride.



Carbon bisulphide.

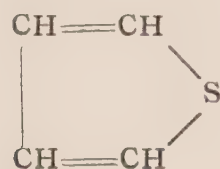
$$\begin{array}{rcl}
 \text{S} = \text{C} = \text{S} & & \\
 V_m & 62.1 & \\
 \text{C} & 14.8 & \\
 2 : \text{S} & 47.2 & \\
 \hline
 \Sigma_n V_a & 62.0 & \\
 V_m & 62.1 & \\
 \hline
 \hline
 \end{array}$$

The reason is probably that the volumes of sulphur are slightly larger than usual, viz. 23.6 by analogy with  $\text{CO}_2$ . This idea is supported by the value found for sulphur in  $\text{PSCl}_3$  22.8.

### Ring Compounds including Sulphur.

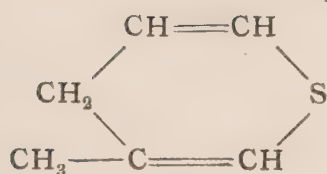
The compounds answering to this description are few in number. They are

Thiophene  $\text{C}_4\text{H}_4\text{S}^{53}$



$$\begin{array}{rcl}
 V_m & 85.1 & \\
 4\text{CH} & 74.0 & \\
 \text{S} & 22.0 & \\
 \hline
 & 96.0 & \\
 \text{less for ring} & -11.0 & \\
 \hline
 \Sigma_n V_a & 85.0 & \\
 V_m & 85.1 & \\
 \hline
 \hline
 \end{array}$$

$\beta$  methyl pent thiophene  $\text{C}_6\text{H}_6\text{S}$

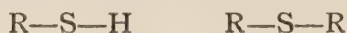


$$\begin{array}{rcl}
 \text{b.p.} & 113.0 & \\
 d_{19} & 0.9935 & \\
 \text{C} & 0.48 \text{ like toluene} &
 \end{array}$$

$$\begin{array}{rcl}
 V_m & 125.9 & \\
 \text{C}_6\text{H}_6 & 118.4 (32 \times 3.7) & \\
 \text{S} & 22.0 & \\
 \hline
 & 140.4 & \\
 \text{less for } \square_6 & -15.0 & \\
 \hline
 \Sigma_n V_a & 125.4 & \\
 V_m & 125.9 & \\
 \hline
 \hline
 \end{array}$$

It is noteworthy that sulphur possesses a volume of only 22.0 in these compounds and not 25.6 as we should expect from a study of the thio ethers. This is different from the results obtained for oxygen and nitrogen.

## The Thio Alcohols (Mercaptans) and Thio Ethers.



The available data are not very numerous, but the conclusions are fairly certain.

## The mercaptans.

Compound.	$V_m$ .	R.	S.
$\text{C}_2\text{H}_5 \cdot \text{S} \cdot \text{H}$	77.6	52.0	25.6
$\text{C}_5\text{H}_{11} \cdot \text{S} \cdot \text{H}$	143.6	117.8	25.8

## The thio ethers.

$\text{CH}_3 \cdot \text{S} \cdot \text{CH}_3$			
$\text{C}_2\text{H}_5 \cdot \text{S} \cdot \text{C}_2\text{H}_5$	121.6	96.0	25.6

It is remarkable that the value for sulphur just indicated is also found in very dissimilar compounds, which include di-, tetra-, and hexavalent sulphur in their composition.

It may further be remarked that the sulphur atom does not seem to exert any special influence on the alkyl radicals, that is, in modifying their atomic volumes, as compared with those found in the normal paraffins. Moreover, no distinction is discoverable between the mercaptans and the thio ethers in regard to their molecular volumes. This is quite different from the results obtained in the series

	$\text{R—O—H}$ $\text{R—NH}_2$	$\text{R—O—R}$ $\text{R}_2\text{=N—R}$	
$\text{S}_2\text{OCl}_4$	b.p. 100	d 1.656	C = 0.45
$\text{Cl} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array} \right\} \text{S—S} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array} \right\} = \text{O}$		$2\text{S} =$	$V_m$ 147.0
		$4\text{Cl}$	51.6
		O	88.4
			8.3
		$\Sigma_n V_a$	148.3
		$V_m$	147.0
		$\Delta$	<u><u>-1.3</u></u> for $\alpha\beta$ structure

This is analogous to tetrachloroacetyl oxide

	$V_m$ 126.0 Th.
$\text{Cl} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array} \right\} \text{C—C} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array} \right\} = \text{O}$	$2\text{C}$ 29.6
	$4\text{Cl}$ 88.4
	O 11.0
	$\Sigma_n V_a$ 129.0
	$V_m$ 126.0
	$\Delta$ <u><u>-3.0</u></u> for $\alpha\beta$ structure

It has been found that there is an increase in volume of +1.5 in  $\text{—CCl : CCl—}$  and similar groups, so that the apparent value of  $\Delta$  is halved. We may suppose that  $\text{S}_2$  may be represented by



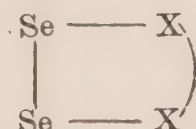
and that sulphur is hexavalent. We do not, however, think that this is the case.

Selenium Se			
Selenyl chloride.			
$\text{SeOCl}_2$			
$\begin{array}{c} \text{b.p. } 179.5 \\ \text{Cl} \\ \diagup \quad \diagdown \\ \text{O} = \text{Se} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array}$	b.p. 179.5	$d_{13} \ 2.443$	$C \ 0.45$
			$V_m \ 79.0$
		$= \text{Se}$	27.0
		$= \text{O}$ $\text{Cl}_2$	9.1 see thionyl chloride 43.2
$\Sigma_n V_a$			79.3
$V_m$			79.0

Selenium chloride			
$\text{Se}_2\text{Cl}_2$			
$\begin{array}{c} \text{b.p. } 169^\circ \\ \text{Cl} \\ \diagup \quad \diagdown \\ \text{Se} = \text{Se} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array}$	b.p. 169°	$d_{17} \ 2.906$	$C \ 0.45$
			$V_m \ 91.4$
		$= \text{Se}$	27.0
		$2\text{Cl}$ $= \text{Se}$	43.2 (2 × 21.6) 21.6
$\Sigma_n V_a$			91.8
$V_m$			91.4

Selenium bromide			
$\text{Se}_2\text{Br}_2$			
$\begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{Se} = \text{Se} \\ \diagdown \quad \diagup \\ \text{Br} \end{array}$			$V_m \ 104.8$
		$= \text{Se}$	27.0
		$= \text{Se}$ $2\text{Br}$	21.6 56.0 (2 × 28.0)
$\Sigma_n V_a$			104.6
$V_m$			104.8

The above three selenium compounds are quite analogous to the corresponding sulphur compounds. For the reasons stated the formula is



excluded. Moreover, selenium is perfectly analogous to sulphur in possessing two values, as must be the case from the nature of the formulæ.

Thus, the first value for  $\text{Se}_1$  is 27.0       $\text{S}_1$  25.6  
and the second value for  $\text{Se}_2$  21.6       $\text{S}_2$  21.6

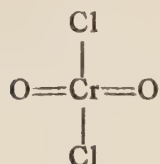
The second is similar in value to that of sulphur.

### Chromium Cr.

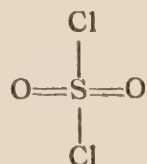
(Thorpe loc. cit.)

Not many chromium compounds have been investigated. Indeed, the only one is chromyl chloride  $\text{CrO}_2\text{Cl}_2$ .

Chromyl chloride.



$\text{CrO}_2\text{Cl}_2$	
$V_m$	88.2
2Cl	43.2
2O	16.6
Cr	28.4
<hr/>	
$\Sigma nV_a$	88.2
$V_m$	88.2
<hr/>	



Chromyl chloride seems perfectly analogous to sulphuryl chloride, and chromium differs from sulphur in possessing a slightly larger volume.

S 25.6      Se 27.0      Cr 28.4

The volume of tellurium is not known, but probably it possesses one of from 37.0 to 40.0.

Elements of Group 5.

	M.W.	$V_m$ .
Oxygen O	16	7.4 under and over 11-12
Sulphur S	32	21.6 25.6
Chromium Cr	52.5	28.4
Selenium Se	78.9	27.0



## CHAPTER VI.

### THE MOLECULAR VOLUMES OF NITROGEN COMPOUNDS.

THE atom nitrogen, perhaps, not even excepting oxygen, is of greatest interest to us, in consequence of its presence in many interesting and useful compounds.

The element nitrogen



Nitrogen being a low boiling-point substance, it may be useful to calculate its value by D. Berthelot's method.

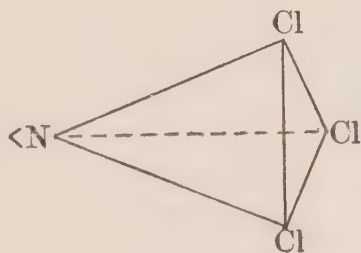
$$T_c \quad 127^\circ \quad P_c \quad 33 \text{ atmos.} \quad T_{b.p.} \quad 78.6$$

$$V_m = \frac{M}{D} = \frac{11.1 \times 127^2}{33 \times (254 - 78.6)} = 30.9.$$

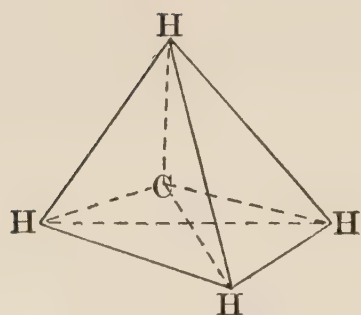
The observed value is

$$V_m \quad 30.9 = 2 \times 15.5.$$

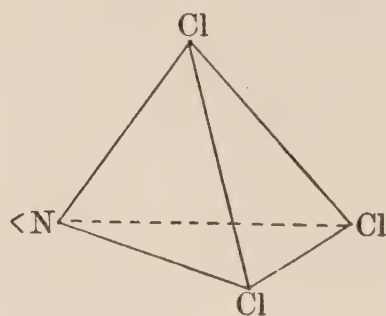
Nitrogen, like phosphorus, is typically a trivalent element, and if we are to judge from the latter, the direction of its valencies when unconstrained are, as in the diagram, along the edges of a tetrahedron.



Such a disposition accounts for the possibility of both nitrogen and phosphorus functioning as pentavalent elements. On comparing the atoms carbon and nitrogen in this respect, we see that carbon cannot assume any higher valency than four—it is saturated, whilst nitrogen may take on two more valencies—it is unsaturated.

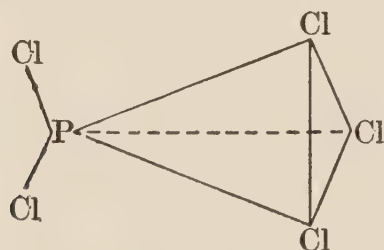
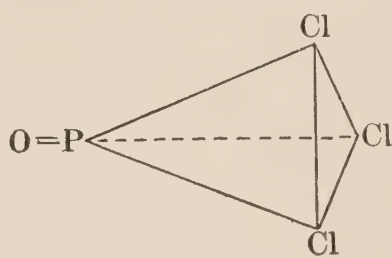
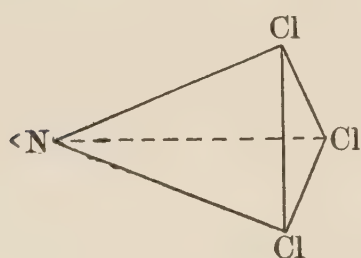


The carbon atom.



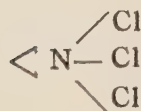
Nitrogen.

The reason for the simultaneous appearance and suppression of the two additional valencies in nitrogen is at once evident. This is further illustrated by the following configurations.



Regarded from the point of view of Barlow and Pope's theory of spatial relationships, we see that in the case of carbon, the molecule is already as compact as possible in such compounds as  $\text{CH}_4$ ,  $\text{CCl}_4$ , etc., and there is no room for additional atoms. In the case of phosphorus, additional atoms can be taken on, and it can function as a pentavalent element. The reasons for the special view which we have taken of nitrogen and phosphorus will be found in the chapter on phosphorus.

Nitrogen trichloride.



$d_0$  1.65      b.p.  $71^\circ$        $C = 0.46$

$V_m$  80.0 (by formula)

N	15.6
3Cl	64.5 ( $3 \times 21.5$ )

$\Sigma_n V_a$	80.1
$V_m$	80.0

It is remarkable that the above value for chlorine is found in such compounds as  $R-Cl$  and  $CH_2Cl_2$ . In this, nitrogen chloride resembles  $PBr_3$ , that is, it possesses the minimum value for the halogen element found in ordinary compounds. The volume of bromine in  $PBr_3$  is also that found in the alkyl bromides  $R-Br$ .

### The Cyanides or Nitriles.

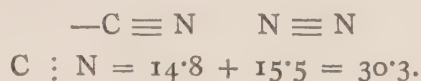


These compounds belong to the class known as unsaturated, and it will be found that the volume of nitrogen in them is normal.

TABLE LXXI.—THE VOLUMES OF THE ALKYL CYANIDES.

Compound.	$V_m$ .	$\Sigma_n V_a(R)$ .	CN.	b.p.
$(CN)_2$ . . . .	60.4	—	30.2	21.0
$CH_3 \cdot CN$ . . . .	57.3	26.0	31.3	81.6
$C_2H_5 \cdot CN$ . . . .	78.5	48.0	30.5	98.0
$C_3H_7 \cdot CN$ . . . .	100.0	70.0	30.0	118.5
Mean value . . . .			30.5	

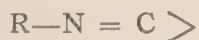
The group CN resembles the combination  $N_2$  in its constitutive features, and might thus be expected to show a similar volume in the case of combined nitrogen.



It has already been shown that

$$N : N = 30.9 = 2 \times 15.5.$$

Isomeric with the nitriles, we find the carbylamines or isocyanides.



In these compounds, carbon appears to be diatomic as in  $< C = O$ . They will be considered after the amines.

### Cyanic Acid and Esters.

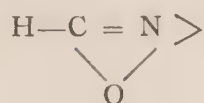


The compound is only stable below  $0^\circ$ .





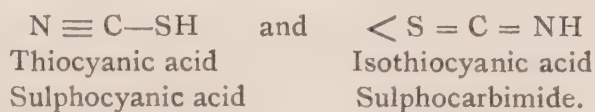
with so-called cyanic acid would lead us to suppose that it has a different structure from that indicated by the ordinary formula (marked II). The only possible one, according to the data, is



The instability of the compound, and the tendency to modification, might lead us to suppose that the ring compound is transformable into the open chain one and *vice versa*. When however, the hydrogen is replaced by an alkyl group, the latter fixes the constitution and the cyanetholins result. The transition to the second group of compounds, chief of which are the isocyanates, probably demands and points to an "intermediate" compound, involving ring structure. This condition is satisfied by Formula I for cyanic acid.

### Thio Compounds.

There are, corresponding to the oxygen compounds, the following combinations with sulphur.



Hydrocyanic acid HCN at the boiling-point  $27^\circ$  possesses a volume of 38.8.

HCN	38.8
CN	30.2
	<hr style="width: 50%; margin: 0 auto;"/>
H	8.6
	<hr style="width: 50%; margin: 0 auto;"/>

This enormous volume for hydrogen is what we should expect. On this basis the volume of CNSH would be

HCN	38.8
S	22.0
	<hr style="width: 50%; margin: 0 auto;"/>
HCNS	60.8
	<hr style="width: 50%; margin: 0 auto;"/>

Clasen gives the density of ( $d_{10}$ ) 1.0013 for what is called hydrosulphocyanic acid

$$\text{or } V_m \text{ } 58.9$$

so that we see that the constitution is that of an open-chain compound, perhaps  $\text{HS} \cdot \text{C} \equiv \text{N}$ . However this may be, thio-

cyanic acid gives rise to esters, which have been well studied, and which possess the formula



The hypothetical  $\text{HN} = \text{C} = \text{S} >$  has derivatives called thiocarbimides  $\text{R}-\text{N} = \text{C} = \text{S} >$

The sulphocyanides.

Methyl sulphocyanide.

$\text{CH}_3\text{S} \cdot \text{C} : \text{N}$	$V_m$ 78.2
$\text{CH}_3$	26.0
$\text{S}$	22.0
$\text{CN}$	30.2
<hr/>	
$\Sigma_n V_a$	78.2
$V_m$	78.2
<hr/>	

Ethyl sulphocyanide.

$\text{C}_2\text{H}_5\text{S} \cdot \text{C} : \text{N}$	$V_m$ 100.1	
$\text{C}_2\text{H}_5$	48.0	b.p. 146
$\text{S}$	22.0	
$\text{CN}$	30.2	
<hr/>		
$\Sigma_n V_a$	100.2	
$V_m$	100.1	
<hr/>		

We see that these compounds give results in perfect accord with their formulas.

Isothiocarbimide  $\text{CS} : \text{NH}$  is not known, but some of its esters, the mustard oils,  $\text{S} = \text{C} = \text{NR}$  are.

We only give details of the ethyl ester in this place; the others are dealt with after the amines for reasons to be given later.

Ethyl thiocarbimide.

$\text{C}_2\text{H}_5\text{N} : \text{C} : \text{S}$	b.p. 133°	$V_m$ 99.3
$V_m$	99.3	
$\Sigma_n V_a$	100.2	
<hr/>		
	-0.9	
<hr/>		

There is thus a difference of 13° between the boiling-points of the two isomers, and a difference in volume of 0.9. The thiocarbimides possess the lowest boiling-points and the smallest volumes.

The carbylamines give rise to the isocyanates or carbimides.

Ethyl carbimide  $\text{C}_2\text{H}_5-\text{N} = \text{C} = \text{O}$

b.p. 60°  $d_{10}$  0.8981  $C = 0.55$

$V_m$  85.5

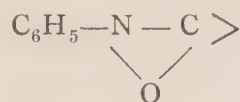
$\text{C}_2\text{H}_5$  48.0  
 $\text{CN}$  30.2  
 $\text{O}$  7.4

$\Sigma_n V_a$  85.6  
 $V_m$  85.5 by formula

Phenyl carbimide	$C_7H_5NO$
b.p. $163^\circ$	$d_{50} \ 1.092$
	$C = 0.45$ from
	$V_m \ 121.7$ phenylthiocarbimide
	$C_6H_5 \ 92.8$
	$CN \ 30.2$
	$O \ 7.3$
	<hr/>
	$130.3$
less for attach. to $C_6H_5$	$-1.4$
	<hr/>
	$\Sigma_n V_a \ 128.9$
	$V_m \ 121.7$
	<hr/>
	$\Delta \ -7.2$
	<hr/>

Whilst ethyl carbimide is apparently normal, in that it possesses the open-chain formula, and so all the alkyl carbimides, phenyl carbimide, on the other hand, seems to possess abnormal structure.

This is indicated by the large minus difference, and shows that there is a three-membered ring in the molecule of phenyl carbimide. Such a formula as that indicated in the preceding scheme would be suitable. We must then suppose that phenyl carbimide possesses the structure shown by the formula



It will be seen that the other aromatic compounds of this nature are quite normal.

TABLE LXXII.

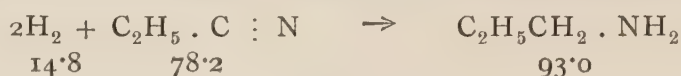
Compounds.	$V_m$ .	$\Sigma_n V_a - R$ .	$\Delta$ .	b.p.	C.
$C_6H_5 \cdot C : N \ . \ .$	121.6	123.0	-1.4	—	—
$C_6H_5 \cdot N : C > \ . \ .$	121.7	123.0	-1.3	—	—
$C_6H_5 \cdot S \cdot C : N \ . \ .$	143.4	145.0	-1.6	$131^\circ$	—
$C_6H_5 \cdot N : C : S \ . \ .$	143.6	145.0	-1.4	$219.8$	$0.45$

Thus there is for the above compounds a contraction of  $-1.4$ , owing to the attachment of the unsaturated groups to the nucleus.

### The Amines.

The amines are derived from the cyanides or nitriles by the addition of nitrogen.

There is in the process of reduction a remarkable contraction.

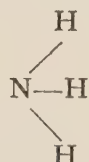


The real volume of propyl amine is

$$\begin{array}{l} \text{C}_3\text{H}_7\text{NH}_2 \quad V_m \ 85\cdot2 \\ \Delta = 85\cdot2 - 93\cdot0 = -7\cdot8. \end{array}$$

Reduction in the cyanides thus produces a contraction.

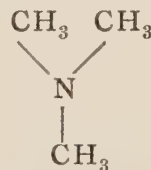
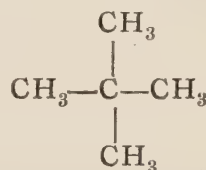
The starting-point of the amines is ammonia.



	$V_m$	26·9
N		15·8
3H		11·1
		<hr/>
$\Sigma nV_a$		26·9
$V_m$		26·9
		<hr/>

This maximum value of nitrogen is preserved in such simple compounds as  $\text{NH}_3$ ,  $\text{NCl}_3$ ,  $\text{N} \equiv \text{N}$ , etc., and in the complex tertiary amines, as will be shown.

In considering the amines we are met with the feature of a divided chain. This can be seen from the plane formulæ



There are important points of difference, however, between these two classes of compounds.

TABLE LXXIII.—THE PARAFFINS.

	b.p.	$\Delta$ .	V.	$\Delta$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	1°		96·0	
		-18		
$\text{CH}(\text{CH}_3)_3$	-17			
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	38	-8	117·8	
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$	30	-28	117·4	-0·4
$\text{C}(\text{CH}_3)_4$	10			
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	71	-9	139·9	-0·5
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2(\text{CH}_3)_2$	62	-7	139·4	
$\text{CH}_3 \cdot \text{CH}(\text{C}_2\text{H}_5)_2$	64	-13		-3·1
$(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{CH} \cdot (\text{CH}_3)_2$	58	-28	136·8	-1·0
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_3$	43	-23	138·9	
	or 48			



It is seen that the boiling-point becomes depressed as the hydrocarbon chain becomes more and more branched. The volume is correspondingly diminished. Additional data are however, urgently needed.

TABLE LXXIV.—THE AMINES.

	b.p.	$\Delta$ .	V.	
$\text{H}_2\text{NC}_2\text{H}_5$	18°		64·6	
$\text{HN}(\text{CH}_3)_2$	7·2	-10·8		
$\text{H}_2\text{NC}_3\text{H}_7$	49·0		85·7	
$\text{N}(\text{CH}_3)_3$	3·5	-35·5	88·0	+2·3
$\text{H}_2\text{NC}_4\text{H}_9$	76·0		106·8	
$\text{HN}(\text{C}_2\text{H}_5)_2$	56·0	-20·0	109·3	+2·5
$\text{H}_2\text{N}(\text{C}_6\text{H}_{13})$	130·0		148·0	
$\text{N}(\text{C}_2\text{H}_5)_3$	89·0	-41·0	152·6	+4·6

The results of the above table show, that, whilst the boiling-points of the two series of compounds diminish as the chain becomes branched, the series varies as regards volume. In the paraffin series the volumes contract as branching occurs, in the amines they expand as a result of this circumstance. In the first series, the boiling-points and the volumes vary in the same sense, among the amines in opposite senses. This at least shows that the boiling-points are not always a guide as to the manner in which the volumes will change. We now examine the volumes in order to ascertain, if possible, the modes of increase.

We have already made use of the principle of constant relative volumes, for example, in discussing propyl and allyl alcohols. We now apply it to a discussion of the amines. It may be stated in passing that, until this principle was applied to this group of compounds, the volume relations appeared very perplexing, and the results not very trustworthy. As we shall see by its utilization, nearly all the difficulties vanish.

If we consider propyl and allyl amines, we find

	$V_m$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{NH}_2$	85·7
$\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{NH}_2$	78·5
	<hr/>
$\Delta$ for $\text{H}_2$	7·2 ( $2 \times 3·6$ )
	<hr/>

$N(C_3H_7)_3$	222.53
$N(C_3H_5)_3$	200.70
<hr/>	
6H	21.83 ( $6 \times 3.638$ )
<hr/>	
$N(CH_3)_3$	88.0
$N(C_2H_5)_3$	152.6
<hr/>	
$3CH_2$	64.6
$CH_2$	21.6 ( $6 \times 3.60$ )
<hr/>	

We thus notice once again the familiar relations

$$CH_2 = 6H \quad C = 4H \quad H = 3.60$$

Among the primary amines we also find that the following similar value holds.

	$V_m.$
$C_2H_5NH_2$	64.6
$C_3H_7NH_2$	85.7
<hr/>	
$CH_2$	21.1

The relations already indicated will enable us to ascertain the volume of nitrogen in the three series of amines.

	$V_m.$	$\Sigma_n V_a(R).$	N.	b.p.
$C_2H_5NH_2$	64.6	54.0	10.6	18
$C_3H_7NH_2$	85.7	75.6	10.1	49
$C_2H_5 \cdot NH \cdot C_2H_5$	109.3	97.2	12.1	7.2
$N(CH_3)_3$	88.0	75.6	12.4	3.5
$N(C_2H_5)_3$	152.6	140.4	12.2	89
<hr/>				
$3CH_2$	64.6			
$CH_2$	21.53			
$N(C_3H_7)_3$	222.53	207.36	15.17	156.5
$N(C_3H_5)_3$	200.70	185.54	15.16	155.5
<hr/>				
6H	21.83			
H	3.638			

The values are apparently from 10-11 in the primary amines, 12-15 in the secondary and tertiary; the volume of the nitrogen atoms thus varies in volume in the different compounds.

There are many peculiarities connected with this series, and one of the chief is the unexplained value for nitrogen. The most useful point of view in which to regard the amines is to compare them with the alcohols and ethers.

Alcohols.	$V_m$ .	Primary amines.	$V_m$ .
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	101.8	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	107.4
		Secondary amines.	
		$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_3$	109.3
The ethers.		Tertiary amines.	
		$\text{CH}_3$	
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_3$	105.0	$\text{CH}_3 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{CH}_3$	109.6
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_3$	106.3	$\text{CH}_3 \cdot \text{N}(\text{CH}_3)_2 + \text{CH}_2$	

We notice that the amino group ( $\text{NH}_2$ ) is similar to the hydroxyl ( $\text{OH}$ ) group, in that it occasions the smallest volume, when in the terminal position. As oxygen becomes situated more and more within the molecule, the volume increases, so with nitrogen. Moreover there is an additional increase as nitrogen becomes the centre for the attachment of three carbon atoms.

It becomes more and more evident, as we study the subject, that we must suppose the typical atoms O, N, S, etc., to produce specific effects\* on the hydrocarbon radicals and other groups with which they are combined. These result in modifications of the individual atomic volumes of such groups, whilst as a rule the relative atomic volumes are preserved. Thus we have shown that the value  $V/W$  measures the volumes of the hydrogen atoms or equivalents in the different series. If now we consider similar terms of the different series



we shall find different values of  $V/W$ . Moreover, the shape of the different curves may not be quite the same, or they will differ in some particular.

If we take the normal paraffin series as the standard, and consider the value of the radicals  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$  derived therefrom as the reference values, we shall, on considering other series, sometimes find that those which we have to attribute to these groups are different. It may also be true that only certain parts of molecules are affected by constitutive influences. In any case, we must consider that variations from the normal are due to the specific influences of certain atoms or groups, as

\* These influences are not necessarily direct, but in any case the atoms N or O or the reactive groups containing them are the causes of such effects.



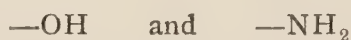
well as to differences of arrangement. The constitutive influences in question will affect the volumes and probably the boiling-points. These definite statements are the outcome of the work done on the nitrogen compounds, especially the amines, and are considered to be of the first importance.

It is seen that the primary amines are considerably diminished in volume as compared with the corresponding secondary and tertiary compounds. In this they are analogous to the alcohols as compared with the alkyl ethers.

As we have seen, there is a contraction of  $-7.5$  approximately, when the cyanides are transformed into the amines by reduction.

Similarly, there are contractions of  $-1.5$  to  $-3.5$  when the aldehydes and ketones are transformed into primary and secondary alcohols by reduction.

We have considered these diminutions in volume as involving only the nitrogen or oxygen atoms, but it is possible that all the atoms in the groups



may be concerned. In any case the constitutive effects are probably due to the oxygen and nitrogen atoms respectively.

The alcohols and the primary amines may also be shown to be similar in many other respects, but it may be noted that the low relative value of the primary amines and the alcohol is connected with the terminal position of the reactive groups  $\text{NH}_2$  and  $\text{OH}$ .

It is to be remarked that the atomic volumes of nitrogen and oxygen both reach a maximum in the simplest compounds, become depressed as the complexity increases, and finally reaches about the maximum value in complex symmetrical amines and ethers respectively.

	$V_m.$	O.		$V_m.$	N.
$\text{H}-\text{O}-\text{H}$	18.5	11.1	$\text{NH}_3$	26.9	15.8
$\text{CH}_3-\text{O}-\text{CH}_3$	62.1	10.1	$\text{N}(\text{CH}_3)_3$	88.0	12.4
$\text{C}_3\text{H}_7-\text{O}-\text{C}_3\text{H}_7$	151.3	11.4	$\text{N}(\text{C}_3\text{H}_7)_3$	222.5	15.2
$\text{C}_4\text{H}_9-\text{O}-\text{C}_4\text{H}_9$	197.6	11.3			

The volumes of amines with iso-groups.

	$V_m.$	$\Sigma_n V_a(R) - 0.5.$	$\Delta.$	b.p.
$(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2\text{NH}_2$	106.3	103.7	$-2.3$	$68^\circ$
$(\text{CH}_3)_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{NH}_2$	127.0	129.4	$-2.4$	$95^\circ$



There is in this class of compounds a depression of about  $-2.4$ .

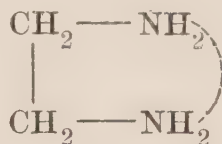
### Compounds Allied to the Amines.

Ethylene diamine.

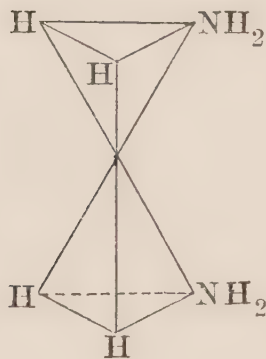
$\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$	b.p. $116.5^\circ$	$d_0$	0.902
$V_m$	75.0		
$2\text{CH}_2$	43.2 ( $12 \times 3.6$ )		
$2\text{NH}_2$	35.6 ( $2 \times 17.8$ )		
$\Sigma_n V_a$	78.8		
$V_m$	75.0 by formula		
$\Delta$	<u><u><math>-3.8</math></u></u>		

The large contraction which has been associated with  $\alpha\beta$  compounds is here again evident.

The formula is



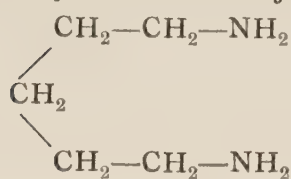
or



and the contraction is an expression of the effect due to the contiguity of the  $\text{NH}_2$  groups.

Propylene diamine  $\text{C}_3\text{H}_6(\text{NH}_2)_2$

	b.p. $120^\circ$	$d_{15}$	0.878	$C = 0.50$
				$V_m$ 95.5
$\text{CH}_3 - \text{CH} - \text{NH}_2$		$\text{C}_3\text{H}_6$	64.8 ( $3 \times 21.6$ )	
$ $		$2\text{NH}_2$	35.6 ( $2 \times 17.8$ )	
$\text{CH}_2 - \text{NH}_2$		$\Sigma_n V_a$	100.4	
		$V_m$	95.5	
		$\Delta$	<u><u><math>-4.9</math></u></u>	

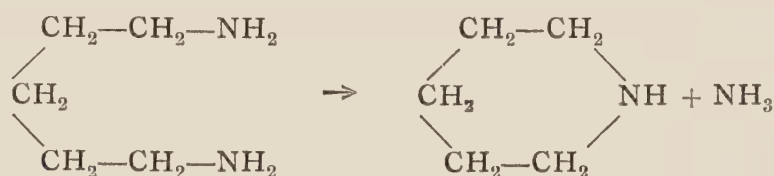
Pentylene diamine  $C_5H_{10}(NH_2)_2$ b.p.  $179^\circ$      $d_0$  0.9174 $V_m$  134.4
$$\begin{array}{r}
 C_5H_{10} \quad 108.0 \\
 2NH_2 \quad 35.6 \\
 \hline
 \end{array}$$

$$\begin{array}{r}
 \Sigma_n V_a \quad 143.6 \\
 V_m \quad 134.4 \\
 \hline
 \end{array}$$

$$\begin{array}{r}
 \Delta \quad -9.2 \\
 \hline
 \end{array}$$

From these calculations we see that there are large contractions connected with  $\alpha\beta$ ,  $\alpha\gamma$ ,  $\alpha\delta$ , etc., compounds. These have been considered in the main to be due to a curvature of the hydrocarbon chains, owing to the close approximation of the two amino groups.

That this is so, is shown by a possibility of the formation of ring compounds from the diamines. For instance, by the splitting off of ammonia, the rings become closed and the cyclic alkylene imides are formed.

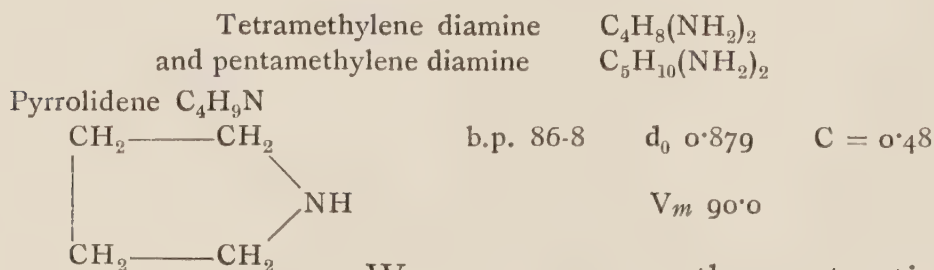


It is doubtful, however, if the whole of the contractions shown above are due to a curvature of the chain.

Dimethylene compounds     $C_2H_4X_2$      $\Delta = -3.1$ Trimethylene    „     $C_3H_6X_2$      $\Delta = -4.5$ 

Then in pentamethylene    „     $C_5H_{10}X_2$      $\Delta = -(3.1 + 3 \times 1.5)$   
 $= -7.5$

The following is a study of the ring compounds pyrrolidene  $C_4H_9N$  and piperidine  $C_5H_{11}N$ , which are derived from the diamines.

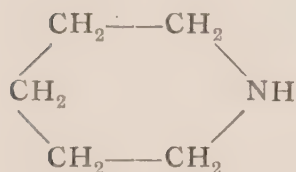


We now compare the contractions obtained on the basis of the values  $H = 3.7$  and  $3.6$  respectively.

4CH <sub>2</sub>	88.4 (4 × 22.1)
N	12.0
H	3.6

Σ <sub>n</sub> V <sub>a</sub>	104.0
V <sub>m</sub>	90.0

$$\Delta \text{ for } \square_5 = -14.0$$

Pipridene C<sub>5</sub>H<sub>11</sub>N

4CH <sub>2</sub>	86.4 (4 × 21.6)
N	12.0
H	3.6

Σ <sub>n</sub> V <sub>a</sub>	102.0
V <sub>m</sub>	90.0

$$\Delta \text{ for } \square_5 = -12.0$$

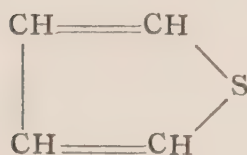
V<sub>m</sub> 108.8 (Schiff)

5CH <sub>2</sub>	108.0
N	12.0
H	3.6

Σ <sub>n</sub> V <sub>a</sub>	123.6
V <sub>m</sub>	108.8

$$\Delta \text{ for } \square_6 = -14.8$$

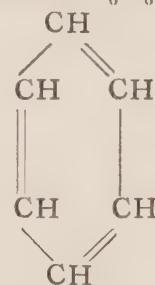
The calculation for pyrrolidene which shows a value of 12 is the correct one, since it contains a five-membered ring. From this we see that in the diamines the volume of CH<sub>2</sub> = 21.6 and not 22.1.

Thiophene C<sub>4</sub>H<sub>4</sub>SV<sub>m</sub> 85.0 (Schiff).

4CH	74.0 (4 × 18.5)
S	22.0

Σ <sub>n</sub> V <sub>a</sub>	96.0
V <sub>m</sub>	85.0

$$\Delta \text{ for } \square_5 = -11.0$$

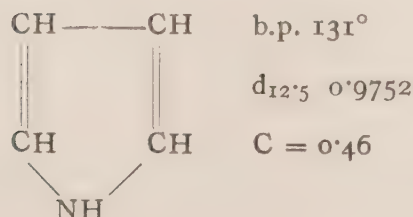
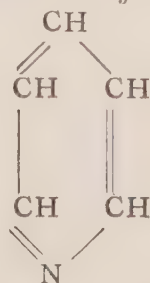
Benzene C<sub>6</sub>H<sub>6</sub>V<sub>m</sub> 96.0

6CH	111.0
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V<sub>m</sub> 96.0

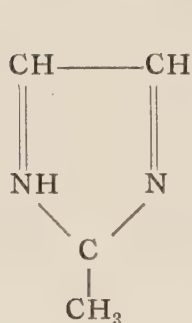
$$\Delta \text{ for } \square_6 = -15.0$$

These numbers agree with those found on the basis of the diminished values of V/W or the hydrogen equivalent. This rule apparently does not apply to the unsaturated ring compounds.

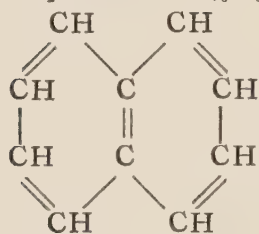
Pyrrol C<sub>4</sub>H<sub>5</sub>NPyridene C<sub>5</sub>H<sub>5</sub>N

$V_m$	79.4
$C_4H_4$	75.0
H	3.6
N	12.0
	<hr/>
	90.6
less for $\square_5$	-11.0
	<hr/>
$\Sigma_n V_a$	79.6
$V_m$	79.4
	<hr/>

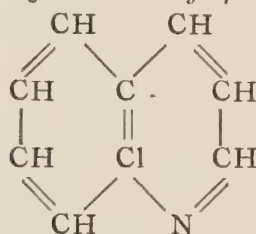
$V_m$	108.8 (Schiff)
$C_5H_5$	92.5
N	12.0
	<hr/>
	104.5
less for $\square_6$	-15.0
	<hr/>
$\Sigma_n V_a$	89.5
$V_m$	89.5
	<hr/>

Methyl glyoxylin  $C_4H_6N_2$ b.p.  $199^\circ$   $d_{20}$  1.0363 $C = 0.46$ 

$V_m$	93.8
$C_4H_6$	81.4
N	24.0
	<hr/>
	105.4
less for $\square_5$	-11.0
	<hr/>
$\Sigma_n V_a$	94.4
$V_m$	93.8
	<hr/>

Naphthalene  $C_{10}H_8$ 

$V_m$	147.2
$C_{10}H_8$	177.6 ( $48 \times 3.7$ )
less for ring	-30.4
	<hr/>
$\Sigma_n V_a$	147.2
$V_m$	147.2
	<hr/>

Quinolene  $C_9H_7N$ 

$V_m$	140.0
$C_9H_7$	159.1 ( $43 \times 3.7$ )
N	12.0
	<hr/>
	171.1
less for ring	-30.4
	<hr/>
$\Sigma_n V_a$	140.7
$V_m$	140.0
	<hr/>

A few additional ring compounds will be dealt with at the end of the present chapter.

It will be observed that we have found a value for nitrogen similar to those derived from the secondary and tertiary amines. This is analogous to the results obtained for rings including oxygen and the volume of this atom was found to be similar to the values derived from the ethers. We find in this fact one more analogy between the amines and the ethers.

We now turn our attention to another class of compounds, the carbylamines, the isocyanates, and the thiocarbimides.



It will be noticed that they all have one feature in common.

Carbylamines	$R-N=C>$
Isocyanates	$R-N=C=O$
Thiocarbimides	$R-N=C=S$

This feature is, that the alkyl groups are in every case attached to nitrogen. They may thus be regarded as derivatives of the amines. As such, the alkyl groups are likely to suffer the contractions already noticed, these being due to the interaction with the atom nitrogen, that is,  $CH_2 = 21.6$  and not  $22.1$ .

In order to facilitate comparisons, we give in the following table, not only members of the series just indicated, but also those of the isomeric compounds in which the alkyl groups are attached to the carbon or sulphur atoms.

TABLE LXXV.

Cyanides. R . C : N	b.p.	$V_m$ .	$\Delta$ .	$V_m$ .	b.p.	Carbylamines. R—N : C >
$C_2H_5 . C : N$	97°	78.4	-1.2	77.2	79.0°	$C_2H_5 . N : C >$
Cyanates or cyanetholens. R . O . C : N		$\Sigma_n V_a$ .		$V_m$ .		Isocyanates. R . N : C : O
$C_2H_5 . O . C : N$	70°	86.9	-1.3	85.6	60°	$C_2H_5 . N : C : O$
Thiocyanates or sulphocyanides. R . S . C : N		$V_m$ .		$V_m$ .		Thiocarbimides. R . N : C : S
$C_2H_5 . S . C : N$	146°	100.1	-0.8	99.3	133°	$C_2H_5 . N : C : S$
$C_3H_5 . S . C : N$	161°	115.0	-1.7	113.3	150.7°	$C_3H_5 . N : C : S$
$C_5H_{11} . S . C : N$	—	166.5	-2.7	163.8	182.0°	$C_5H_{11} . N : C : S$

It is seen that the compounds which possess the



group have lower boiling-points, and consistently smaller volumes. Contractions are thus found which increase as the alkyl groups become more complex. As before indicated, this is probably due to specific actions of the nitrogen atoms on the radicals. The validity of this rule is shown in the following table.

TABLE LXXVI.

Compound.	H 3.6	$CH_2$ 21.6		
$C_2H_5 . N : C >$	$V_m$ .	N : C >	+ R	$\Sigma_n V_a$ .
	77.2	30.2	46.8	77.0
$C_2H_5 . N : C : O$	85.6 *	N : C : O	37.6	84.4
		N : C : S		
$C_2H_5 . N : C : S$	99.3	52.4	„	99.2
$C_3H_5 . N : C : S$	113.3	„	61.2	113.6
$C_5H_{11} . N : C : S$	163.8	„	111.6	164.0

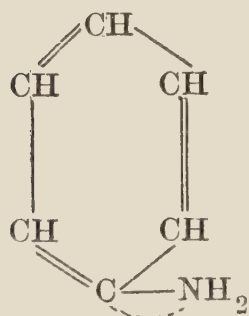
\* The volume of this compound agrees better with the usual value of  $C_2H_5$  48  
 $\Sigma_n V_a$  48.0 + 37.6 = 85.6.

## Aromatic Amino Compounds.

The interesting subject of the possible mutual influence of the phenyl ( $C_6H_5$ ) and amino groups is capable of fairly extended treatment, owing to the extended material which is available. It will be necessary to give detailed calculations in order to illustrate the methods of calculation. The calculation of values by the direct summation of the individual atomic volumes is not advisable when compounds of some complexity are dealt with, but comparisons with closely analogous compounds are preferable.

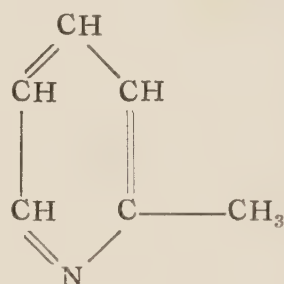
We first compare aniline and picolene, both of which possess the empirical formula  $C_6H_7N$ , but which possess somewhat different molecular volumes.

Aniline  $C_6H_5NH_2$   
 $V_m$  106.6



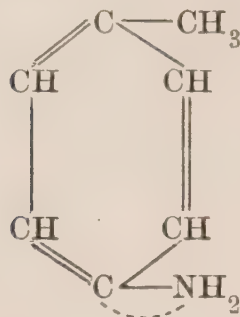
$C_6H_5$	92.8
$NH_2$	17.8
	<hr/>
	110.6
less for const.	-4.0
	<hr/>
$\Sigma_n V_a$	106.6
$V_m$	106.6
	<hr/> <hr/>

$\alpha$  Picolene  
 $V_m$  111.7



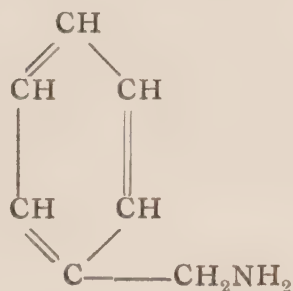
$C_5H_4$	88.8 (24 × 3.7)
$CH_3$	26.0
N	12.0
	<hr/>
$\Sigma_n$	126.8
less for $\square_6$	-15.0
	<hr/>
$\Sigma_n V_a$	111.8
$V_m$	111.7
	<hr/> <hr/>

It is seen that there is a contraction of -4.0 connected with aniline. This is in accord with the rule that when an unsaturated group is attached to the phenyl radical, there are contractions of greater or lesser magnitude. We now investigate a number of compounds similar to aniline, but containing hydrocarbon radicals of different magnitudes.

*p* Toluidineb.p. 201.5  $V_m$  128.9  
(Neubeck)

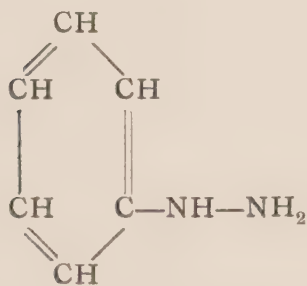
$\text{C}_6\text{H}_4$	89.6
$\text{CH}_3$	25.5
$\text{NH}_2$	17.8
	<hr/>
	132.9
less for const.	-4.0
	<hr/>
$\Sigma_n V_a$	128.9
$V_m$	128.9
	<hr/> <hr/>

## Benzylamine

b.p. 183  $d_{14}$  0.990  
 $V_m$  127.4

$\text{C}_6\text{H}_4$	92.8
$\text{CH}_2$	21.6
$\text{NH}_2$	17.8
	<hr/>
	132.2
less for const.	-4.0
	<hr/>
$\Sigma_n V_a$	128.2
$V_m$	127.4
	<hr/> <hr/>

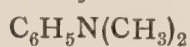
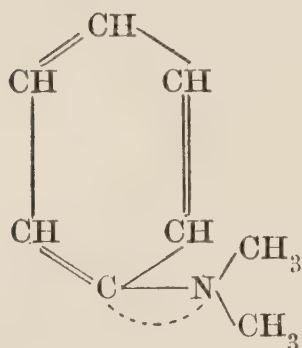
The boiling-point of Neubeck's compound has been taken as 201.5°, but at 198° (the boiling-point usually given), benzylamine has the same volume as *p* toluidine.



$d_{21}$ 1.091	b.p. 241°	$C = 0.45$
	$V_m$ 120.0	
	$\text{C}_6\text{H}_5$	92.8
	$\text{NH}$	14.2
	$\text{NH}_2$	17.9
		<hr/>
		124.9
less for const.		-4.0
		<hr/>
	$\Sigma_n V_a$	120.9
	$V_m$	120.0
		<hr/> <hr/>

From this we conclude that the contractions due to the combination of  $-\text{CH}_2\text{NH}_2$  with the phenyl radical  $\text{C}_6\text{H}_5$  is about the same in value as for  $\text{NH}_2$ .

Dimethyl aniline.


 $V_m$  152.4


92.8

62.8

155.6

less for const.

-4.0

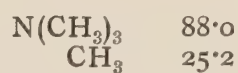
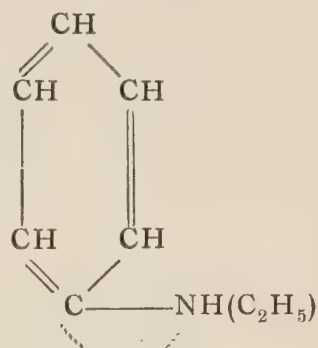
 $\Sigma_n V_a$ 

151.6

151.6 ethyl aniline

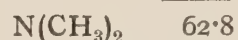
152.4 dimethyl aniline

Ethyl aniline.


 $V_m$  151.6


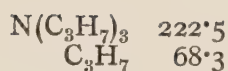
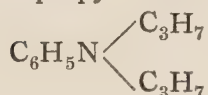
88.0

25.2



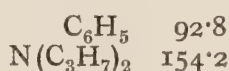
62.8

Dipropyl aniline.



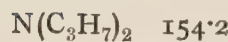
222.5

68.3



92.8

154.2



154.2

less for const.

247.0

-4.0

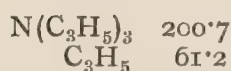
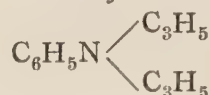
 $\Sigma_n V_a$ 

243.0

 $V_m$ 

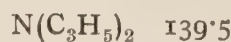
243.6

Diallyl aniline.

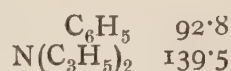


200.7

61.2



139.5



92.8

139.5

less for const.

232.3

-4.0

 $\Sigma_n V_a$ 

228.3

 $V_m$ 

225.7

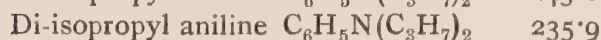
 $\Delta$ 

-2.6

Di-isopropyl aniline.


 $V_m$  235.9


243.6



235.9

 $\Delta$ 

-7.7

It is concluded from the above investigation that there is a contraction of about  $-4.0$ , when the amino or similar radical becomes attached to the benzene nucleus. Moreover it does not apparently matter what the complexity of the substituting hydrocarbon group or groups is, so long as they are saturated. If



unsaturated, in the sense of possessing residual affinity, it seems that the contractions are increased. On this last point, however, we need further information.

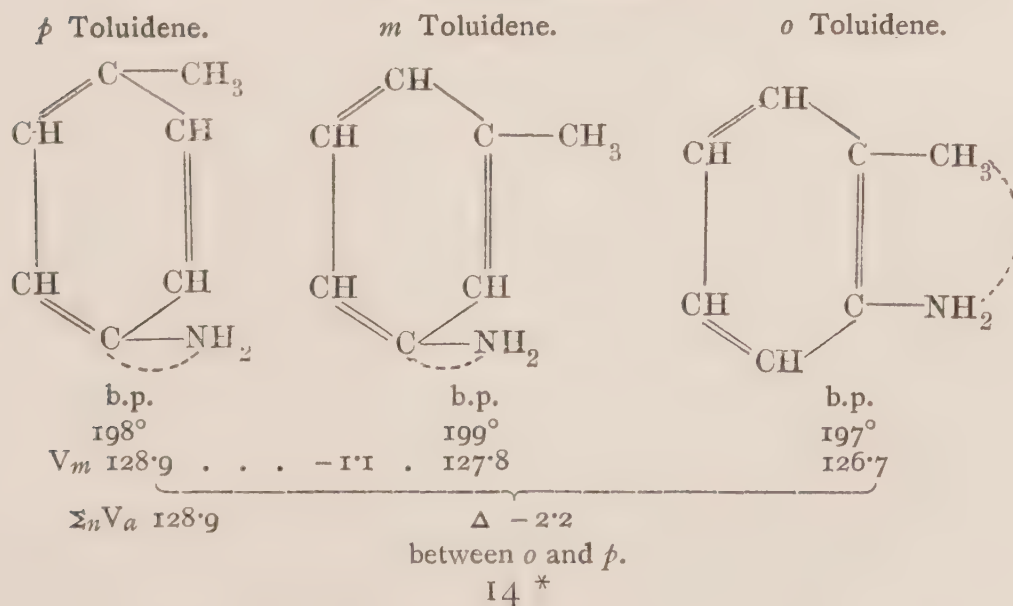
One very interesting point is, that if methylene groups be interposed between the unsaturated radical and the nucleus, it makes no difference to the contraction. We have a sufficient number of instances of this to be certain on this point.

<i>p</i> Cresol. $C_6H_5(CH_3)(OH)$ $C_6H_5 \cdot O \cdot CH_3$	$V_m$ . 123·7 125·2	$V_m - \Sigma_n V_a$ . -1·3	$V_m$ . 123·7	Benzyl alcohol. $C_6H_5CH_2OH$
	$\Sigma_n V_a$	134·9	-1·6	136·5
	$\Sigma_n V_a$	154·5	—	154·7
Benzoic acid + 2CH <sub>2</sub> $C_6H_5 \cdot COOH + 2CH_2$	170·9	-3·8	170·9	
<i>p</i> Toluidene. $C_6H_4(CH_3)NH_2$	128·4	-4·0	127·9	
				Benzyl chloride. $C_6H_5CH_2Cl$ not Benzilidene chloride. $C_6H_5CHCl_2$ Phenyl propionic acid. $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH$ Benzylamine. $C_6H_5CH_2NH_2$

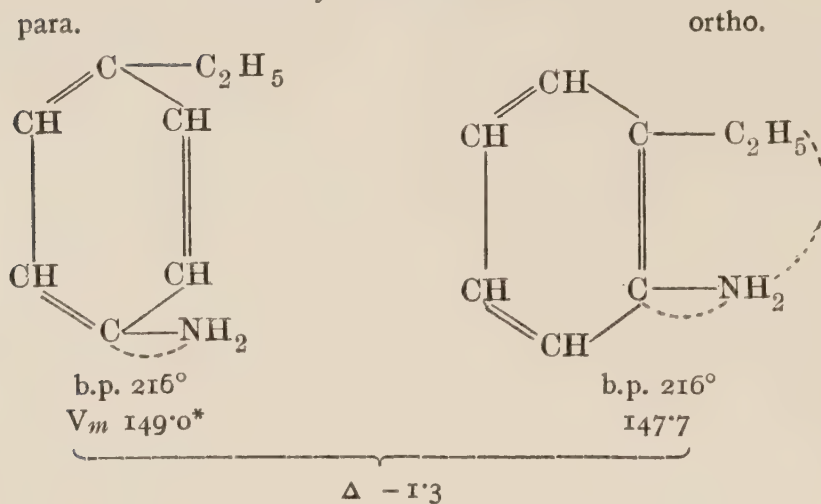
It is difficult to understand why this should be so, unless by a suitable arrangement of the atoms the phenyl and unsaturated groups are brought into proximity. This is probable. Since the amount of the contraction apparently bears some relation to the reactivity of the groups or the number of unsaturated atoms, we must connect these contractions with the residual affinity associated with the unsaturated atoms, that is, with the latent valencies.

We now discuss a number of cases showing interference between contiguous groups.

### The Toluidenes.



## The ethyl amido benzenes.



$C_6H_4$	89.6	less for const.	$153.9$ $-4.0$
$C_2H_5$	46.5	less for <i>o</i> struct.	$149.9$ $-2.2$
$NH_2$	17.8		
	<u>153.9</u>	$\Sigma_n V_a$	$147.7$
		$V_m$	<u><math>147.7</math></u>

## The Xylidenes.

1 : 3 : 4				1 : 3 : 5			
b.p.	$V_m$	$148.6$ (Neubeck)		b.p.	$d_{15}$	$0.972$	$C = 0.52$
$218^{\circ}$				$220$	$V_m$	$151.2$	
	$C_6H_3$	86.4			$C_6H_3$	86.4	
	$2CH_3$	51.0			$2CH_3$	51.0	
	$NH_2$	17.8			$NH_2$	17.8	
		<u>155.2</u>				<u>155.2</u>	
	less for const.	$-4.0$			less for const.	$-4.0$	
		<u>151.2</u>			$\Sigma_n V_a$	$151.2$	
	less for <i>o</i> struct.	$-2.2$			$V_m$	<u><math>151.2</math></u>	
		<u>149.0</u>					
	$\Sigma_n V_a$	$149.0$					
	$V_m$	<u><math>148.6</math></u>					

\* The *m* and even *p* compounds probably suffer appreciable contractions.

## The Oxides and Esters of the Nitrogen Acids.

Nitrous oxides.



This compound boils at the comparatively low temperature of  $186^\circ \text{A}$ .

Its volume at the boiling-point can be calculated by D. Berthelot's formula from the critical data.

$$\frac{M}{D} = V_m = \frac{11.1 T_c^3}{P_c (2 T_c - T)},$$

$P_c$ ,  $T_c$  crit. press. and temperature.

$T$  boiling-point temp.

Compound.	T.	D.	$T_K$ .	$P_K$ (atmos.)	$V_m = \frac{M}{D}$ .	V. calc.
$\text{N}_2$	78.6	0.885	127	33.0	31.6	30.9
$\text{NH}_3$	274.0	0.635	403	115.0	26.9	29.5
$\text{N}_2\text{O}$	183.0	—	309	73.6	—	33.1

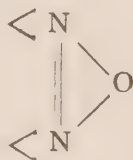
$V_m$  for  $\text{N}_2\text{O}$  is 33.1

$$\begin{array}{r} 2\text{N} \quad 31.6 \quad (2 \times 15.8) \\ \text{O} \quad 8.3 \\ \hline \end{array}$$

$$\begin{array}{r} \Sigma n V_a \quad 39.9 \\ V_m \quad 33.1 \\ \hline \end{array}$$

$$\Delta = -6.8$$

This large difference between the theoretical and experimental values points to ring structure. On considering the type of ring which would be suitable, we find that it is compatible with a three-membered single ring. Thus



This is indeed the only type of structure which is in agreement with our conception of the valency relations of the atoms nitrogen and oxygen. It is the only one which would take into account the well-known trivalent nature of the one atom and divalency of the other.

This result is of extreme importance in accounting for the constitution of the phosphorus oxides.

Nitric oxide



The critical data for this compound are

$$T_c \quad 180^\circ\text{A} \quad P_c \quad 71 \text{ atmos.} \quad T_{b,p.} \quad 120^\circ\text{A.}$$

By D. Berthelot's formula

$$V_m = \frac{M}{D} = \frac{11.1 \times 180 \times 180}{71 \times (360 - 120)} = \frac{359600}{17040} = 21.2.$$

The theoretical volume would be

N	15.6
O	8.2
<hr/>	
$\Sigma_n V_a$	23.8
<hr/>	

The difference is not too great for this kind of calculation.

Nitrosyl chloride.



The data for this compound are

d-15	1.425	b.p.	-5.0°	C	= 0.46
$V_m$	46.7				
N	15.6				
O	8.3				
Cl	22.1				
<hr/>					
$\Sigma_n V_a$	46.0				
$V_m$	46.7				
<hr/>					

Theory and experiment are seen to agree quite well, and also that the divergence from the theoretical value noted in the case of nitric oxide NO, is due to the particular method of calculating it.

We are also certain that the true volume of NO is

NOCl	46.7
Cl	22.1
<hr/>	
NO	24.6
$\Sigma_n V_a$	23.8
<hr/>	

Moreover the formula for nitrosyl chloride cannot be any other than



Nitrogen trioxide.





Data :—

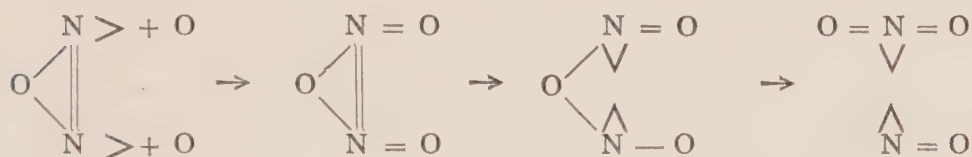
$d_0$	1.449	b.p.	4°
$d_4$	1.437		
$V_m$	53.9		
$N_2$	31.6	(2 × 15.8)	
$3O$	24.9	(3 × 8.3)	
$\Sigma_n V_a$	56.5		
$V_m$	53.9		
$\Delta$	-2.6		

It is seen that a difference of 2.9 exists between theory and experiment. This is not sufficient for us to suppose that there is any great modification in structure from the usual one, but in attempting to find an explanation we notice one remarkable fact, that the sum of the volumes of  $NO_2$  and  $NO$  are almost exactly equal to the experimentally derived volume. In the latter case, however, we must use the volume found by D. Berthelot's formula and not the one agreeing with theory.

$NO_2$	32.0	( <i>v. ante</i> )
$NO$	23.8	
$\Sigma_n V_a$	54.8	
$V_m$	53.6	

This would lead us to suppose that the liquid at 0°, or only four degrees below the point at which it vaporizes and is supposed to decompose, is really a mixture of the two liquids  $NO$  and  $NO_2$ , a supposition which may quite well turn out to be true.

The formation and decomposition would thus be



Possibly all of the above compounds may exist at some temperature or another, and no doubt together in greater or less proportions.

Nitrogen tetroxide

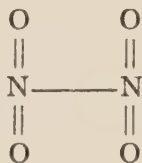


This compound has been actually examined by Thorpe at the boiling-point, and the volume found by him was

$V_m$  64.0 very approx. (63.95 exactly) at the boiling-point 21.6

$N_2$	31.2 (2 × 15.6)
O	33.2 (4 × 8.3)
$\Sigma_n V_a$	64.4
$V_m$	64.0

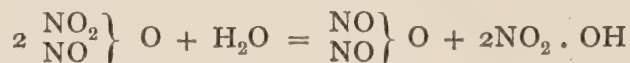
In considering the question of structure we might be led to suppose that its constitution is represented by



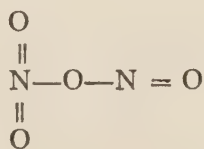
This is especially the case if we note that the volume of the nitro group in the nitro paraffins is half the volume of  $N_2O_4$  or 32.0.

$C_2H_5NO_2$	80.4
$C_2H_5$	48.0
$NO_2$	32.4

Certain observations like the following have led chemists to suppose that it has a different formula.



This is indicated by the one just given, which is—



or a mixture of the oxides of nitrous and nitric acid. This is quite compatible with the molecular volume found by Thorpe

for	NO	24.1 from NOCl.
	NO <sub>2</sub>	32.0 from value in nitro paraffins.
	O	8.3
$\Sigma_n V_a$	64.4	
$V_m$	64.0	

The nitro paraffins.

	$V_m$ .	$\Sigma_n V_a$ .
$CH_3 \cdot NO_2$	59.6	58.0

The volume of the methyl compound in any series is usually larger than that calculated.



This has already been calculated

$\text{C}_2\text{H}_5$	48.0
$\text{NO}_2$	32.0
<hr/>	
$\Sigma_n V_a$	80.0
$V_m$	80.4
<hr/>	

The general formula applicable to these compounds is



The esters of nitrous acid.

		$V_m$ .	b.p.
ethyl nitrite	$\text{C}_2\text{H}_5-\text{O}-\text{N}=\text{O}$	79.2	+ 16°

If we suppose that the oxygen atom in the  $\text{C}_2\text{H}_5-\text{O}-$  group possesses a similar volume to that found in the esters of the carboxylic acids, we obtain the following results:—

$\text{C}_2\text{H}_5$	48.0
$\text{O}$	7.4
$\text{NO}$	23.9
<hr/>	
$\Sigma_n V_a$	79.3
$V_m$	79.2
<hr/>	

The formula is that already given.



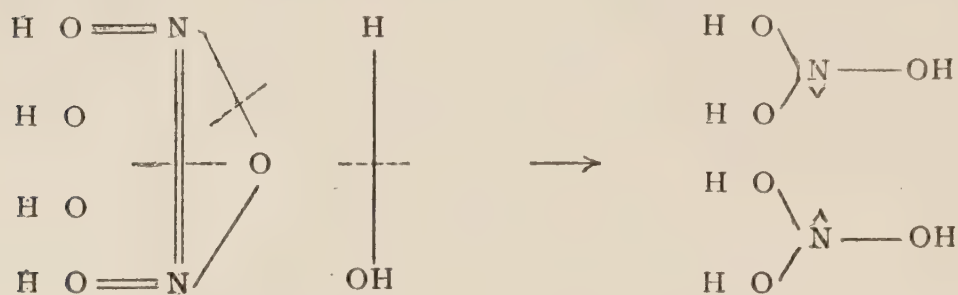
It would be advantageous to possess a larger series of values.

An examination and comparison of the boiling-points shows how large a difference exists between the isomers in this respect.

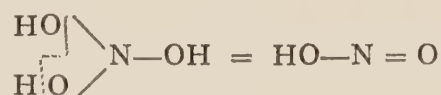
Ethyl nitrite.	b.p.	nitro ethane.	b.p.
$\text{C}_2\text{H}_5-\text{O}-\text{N}=\text{O}$	16°	$\text{C}_2\text{H}_5-\text{NO}_2$	114.5

There is no less a difference than 100 degrees between the boiling-points. In spite of this fact the law of additivity holds. There is also the great probability of the nitro paraffins being associated.

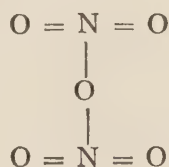
The formation of nitrous acid would be represented thus



Water then splits off



We have no knowledge of the volume of nitrogen pentoxide but its formula is doubtless



United with water this gives

Nitric acid  $\text{HNO}_3$ .

$d_0$  1.54      b.p. 86.       $C = 45^\circ$

$V_m$	45.0
$\text{NO}_2$	32.0
$\text{HO}$	11.0
<hr/>	
$\Sigma_n V_a$	43.0
$V_m$	45.0
<hr/>	

The excess of  $V_m$  over  $\Sigma_n V_a$  is due to the unusually large volume of hydrogen which is found in such compounds. Compare  $\text{HCN}_1$   $\text{HCl}$  etc.

The esters of nitric acid.

		$V_m$ .	b.p.
Amyl nitrate	$\text{C}_5\text{H}_{11}\text{---O---NO}_2$	152.9 (Schiff)	147°
	$\text{C}_5\text{H}_{11}$	114.1	
	$\text{O}$	7.4	
	$\text{NO}_2$	32.0	
	<hr/>		
	$\Sigma_n V_a$	153.5	
	$V_m$	152.9	
	<hr/>		

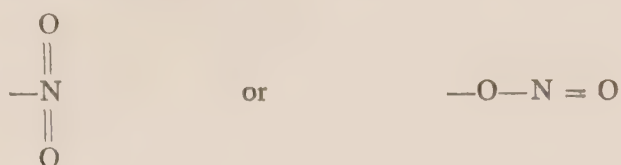
Again the volume of the oxygen atom in



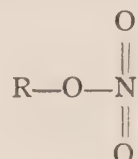
is found to be 7.4 as in the carboxylic esters and acids.



The question now arises whether the constitution of the remaining group  $\text{NO}_2$  is—

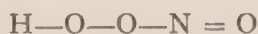


Presumably the formula suited to the nitrates is—



but there is difference of opinion with reference to nitric acid.

Bruhl,<sup>54</sup> from optical data, finds that nitric acid may have a peroxide formula



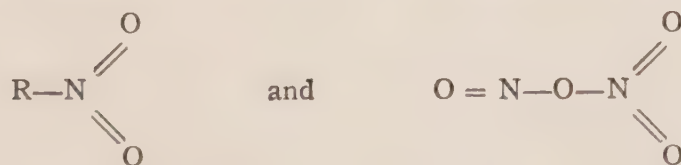
but supposes that the formula represents only one phase of a cycle of changes, of which the formula  $\text{H}-\text{O}-\text{NO}_2$  may be another. Klason and Carlson apparently confirm this view by the detection of the alkyl peroxide in the products of saponification of the alkyl nitrates.

From our present point of view, we may say that there is little or nothing in the way of evidence either for or against this view, since it is probable that the volume of  $\text{HNO}_3$  obtained would fit either formula. The reason is that the volume of the singly bound oxygen attached to nitrogen may not be very different from 8.3, the volume of : O.

### The Aromatic Nitro Compounds.

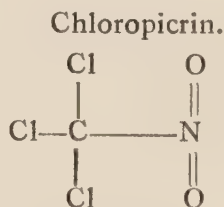
It has been shown that when unsaturated groups are attached to the benzene nucleus, there are considerable contractions.

We have seen that the group  $\text{NO}_2$  possesses a volume of 32.0 units when attached to the alkyl radicals and also in  $\text{N}_2\text{O}_4$ .



If, however, the hydrogen atoms in the methyl group be substituted by chlorine atoms, the conditions are realized for that

interaction between the two groups which might be responsible for a contraction.



$V_m$  110.5 (Thorpe).

$\text{CHCl}_3$	84.5	$\text{CCl}_3$	80.8
H	3.7	$\text{NO}_2$	32.0
<hr/>		<hr/>	
$\text{CCl}_3$	80.8	$\Sigma_n V_a$	112.8
		$V_m$	110.5
		<hr/>	
		$\Delta$	-2.3
		<hr/>	

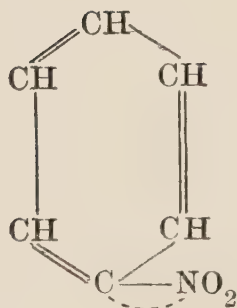
The operating influences are probably derived from the nitrogen atom rather than from the doubly-bound oxygen.

Contractions like the above are shown when the nitro group is united to the benzene nucleus.

Nitro benzene  $\text{C}_6\text{H}_5\text{NO}_2$

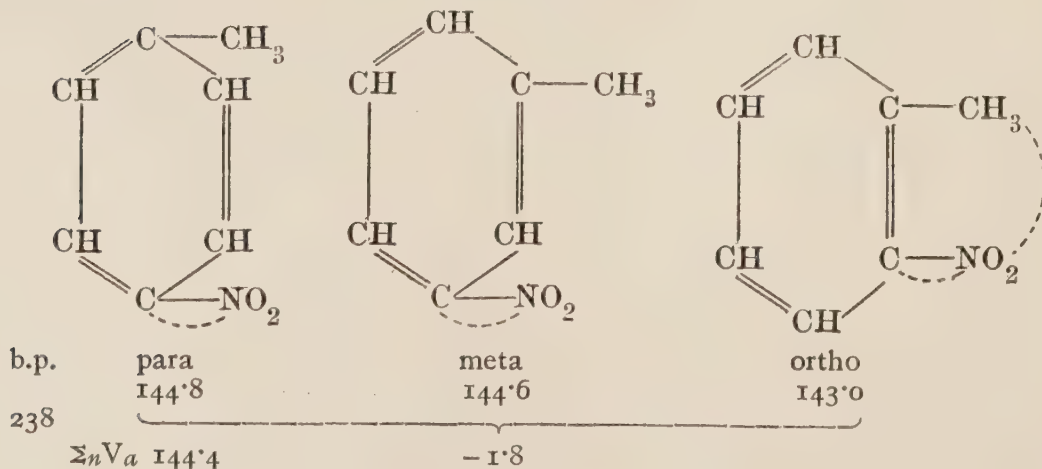
b.p. 208°    d<sub>b.p.</sub> 1.0073

$V_m$  122.1



$\text{C}_6\text{H}_5$	92.8
$\text{NO}_2$	32.0
<hr/>	
$\Sigma_n V_a$	124.8
$V_m$	122.1
<hr/>	
$\Delta$	-2.7 for constitution.
<hr/>	

The nitro toluenes.



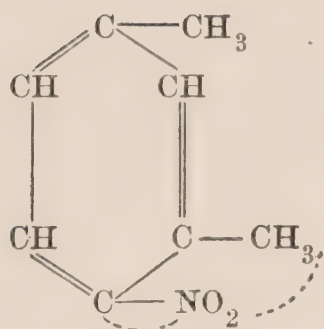
Orthonitro toluene.

$C_6H_4$	89.6
$NO_2$	32.0
$CH_3$	25.8
	<hr/>
	147.1
less for $NO_2$	- 2.7
	<hr/>
	144.4 . . . volume of paranitro toluene
less for <i>o</i> struct.	- 1.8
	<hr/>
$\Sigma_n V_a$	142.6 . . . volume of orthonitro toluene
$V_m$	143.0
	<hr/>

Nitro metaxylene  $C_6H_3(CH_3)_2NO_2$  (1 : 3 : 4)

b.p. 244° db.p. 0.9163

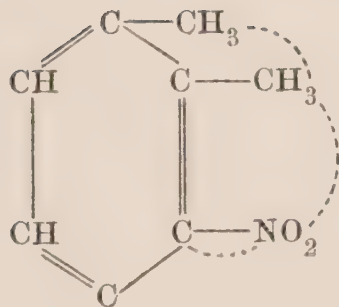
$V_m$  164.8



$C_6H_3$	86.4
$2CH_3$	51.0
$NO_2$	32.0
	<hr/>
	169.4
less for $NO_2$	- 2.7
	<hr/>
	166.7
less for <i>o</i> struct.	- 1.8
	<hr/>
$\Sigma_n V_a$	164.9
$V_m$	164.8
	<hr/>

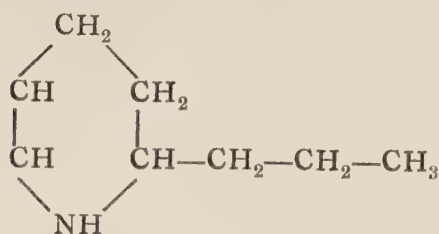
Nitroortho xylene  $C_6H_3(CH_3)_2NO_2$  (1 : 2 : 3)

b.p. 252 db.p. 0.926  $V_m$  163.0



$C_6H_3$	86.4
$2CH_3$	51.0
$NO_2$	32.0
	<hr/>
	169.4
	<hr/>
	169.0
less for $NO_2$	- 2.7
	<hr/>
	166.3
less for <i>o</i> struct.	- 1.8
	<hr/>
	164.5
less for <i>o</i> struct.	- 1.8
	<hr/>
$\Sigma_n V_a$	162.7
$V_m$	163.0
	<hr/>

One or two more ring compounds may now be studied. They are interesting owing to the fact that they are either alkaloids or connected with alkaloids.

Coniine  $C_8H_{17}N$ 

For propyl benzene

$$C_6H_5 \cdot C_3H_7 \quad C = 0.50$$

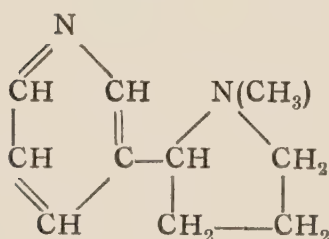
Coniine

$$d_{15} \ 0.850 \quad \text{b.p. } 167^\circ$$

$$V_m \ 175.6 \text{ by formula}$$

The most direct method of calculation is as follows:—

Pipridene	$C_5H_{11}N$	108.8
	$3CH_2$	66.3
	$\Sigma_n V_a$	175.1
	$V_m$	175.6

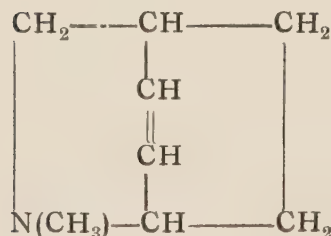
Nicotine  $C_{10}H_{14}N_2$ 

$$\text{b.p. } 247^\circ \quad d_4 \ 1.033$$

$$d_{15} \ 1.011 \quad C = 0.46$$

$$V_m \ 193.1 \text{ by formula}$$

Pyridene	89.3
Methyl pyrrolidin	110.4
	199.7
less 2H	- 6.4
$\Sigma_n V_a$	193.3
$V_m$	193.1

Tropilidene  $C_8H_{13}N$ 

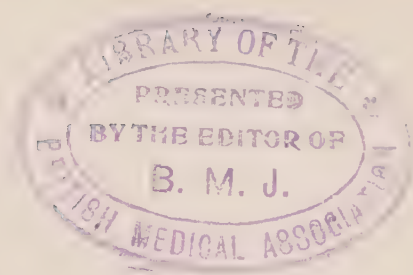
$$d_0 \ 0.9665 \quad \text{b.p. } 162^\circ \quad C = 0.46$$

$$V_m \ 149$$

$C_8H_{13}$	166.5
N	12.0
	178.5
less for ring	- 30.0
$\Sigma_n V_a$	148.5
$V_m$	149.0

The above remarkable series of ring compounds indicates how closely the theory of molecular volumes is able to synthesize the values found by experiment or by calculation by an independent method.





## CHAPTER VII.

### THE MOLECULAR VOLUMES OF PHOSPHORUS COMPOUNDS.

#### The Element Phosphorus.

THE element has a very much smaller volume in the free than in the combined state.

P = 20.9 (Ramsay and Masson)	free
P = 27.0	combined

The complexity of the phosphorus molecule is well known to be



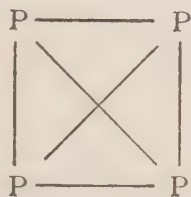
It follows that the molecular volumes are—

	$P_4$ (free)	83.6
Equivalent $P_4$ (combined)		108.0
	$\Delta$	<u>-24.4</u>

This is a large contraction which can only be accounted for by supposing that the phosphorus molecule involves ring structure of a complicated kind. This is difficult to understand, if we consider the nature of this molecule. The simplest assumption, consistent with the valency relations of the phosphorus atom is—



but this would account for a contraction of only - 8.5. A modification of the above



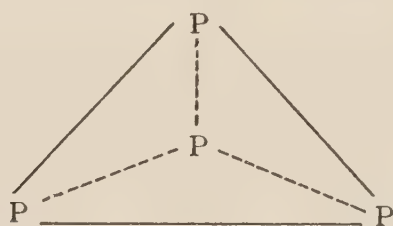
which is equivalent to four three-membered single rings is found

to be suitable. Such a configuration would possess a contraction of

$$4 \times -6.0 = -24.0$$

and this is practically the same as the number just found.

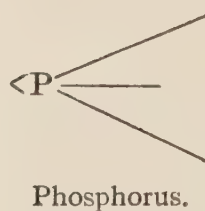
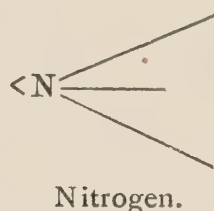
The above formula can be modified in a very interesting and suggestive manner, which is shown in the following diagram.



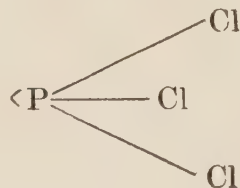
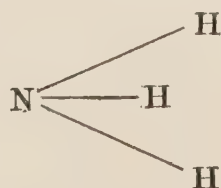
This represents a regular tetrahedron, with an atom of phosphorus at each corner, and the valency linkages directed along the edges of this tetrahedron.

Such a formula explains many facts connected with the combinations of this atom, and also of that of the very similar nitrogen.

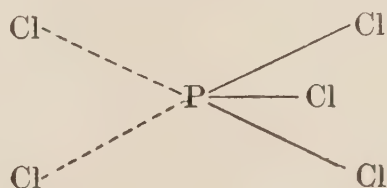
The valency directions of the single atom of either element would be as in the diagram



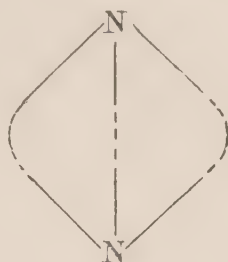
and the formulæ for the chlorides, etc., represented by



From the point of view of their spatial relations, these formulæ at least allow of union with additional atoms, to form compounds which involve pentavalent nitrogen or phosphorus.

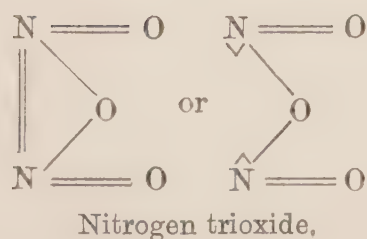
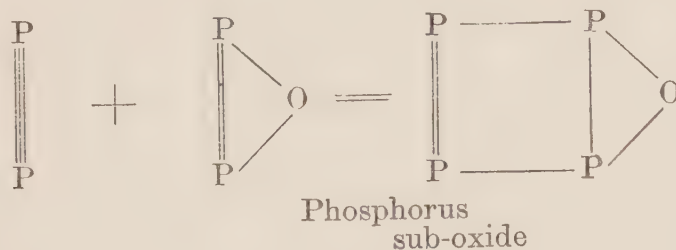
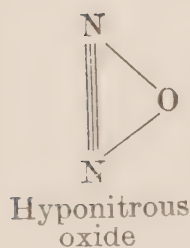
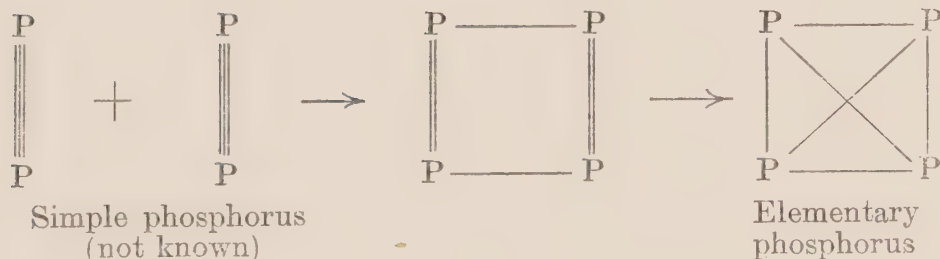


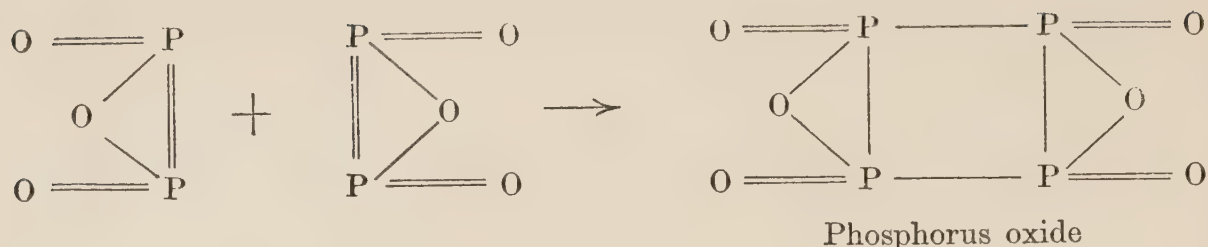
The molecule nitrogen would be represented by



or by a modified formula.

In giving the configurations of certain simple phosphorus combinations, we assume that a molecule of phosphorus  $P_2$  (like  $N_2$ ) is at least theoretically possible, and rely on certain observations on the molecular volumes of nitrogen compounds, and on the recognized empirical formulæ of others, for evidence concerning the genetic relations of the series of phosphorus compounds.





The formulæ for hyponitrous oxide and nitrogen trioxide have been verified by means of molecular volumes. We see from the above formulæ that similar simple compounds occur for phosphorus as for nitrogen but by simple combinations the more complex compounds are found to be possible. The molecular volume of phosphorus oxide might easily be found experimentally. Failing direct data, we calculate the volume of this compound by means of the formula already used.

$  \begin{array}{c} \text{O} \parallel \text{P} \text{---} \text{P} \parallel \text{O} \\ \diagup \quad \diagdown \quad \quad \diagdown \quad \diagup \\ \text{O} \quad \quad \quad \text{O} \\ \diagdown \quad \diagup \quad \quad \diagup \quad \diagdown \\ \text{O} \parallel \text{P} \text{---} \text{P} \parallel \text{O} \end{array}  $		$  \begin{array}{c} \text{PCl}_3 \quad 93.34 \\ \text{POCl}_3 \quad 101.37 \\ \hline \text{O} = \quad 8.0 \\ \hline \hline \end{array}  $	
4P	108.0 (4 × 27.0)		
6O	48.0 (6 × 8.0)		
	<hr/>		
	156.0		
less for $\square_4$	-8.5		
	<hr/>		
	147.5		
less for 2 $\square_3$	-13.0		
	<hr/>		
$\Sigma_n V_a$	<u>134.5</u>		
	<hr/>		
$d_{25}$ 1.936	b.p. 173.1°	C = 0.50	
	$V_m$ 132.5		

The difference between the two numbers  $V_m$  and  $\Sigma_n V_a$  is comparatively small. At any rate, it is satisfactory to find that there is ample evidence for a large contraction due to more or less complicated ring structure. ( $\Delta = -23.5$  as against  $-21.5$ .)

Thorpe has determined the volumes of a number of phosphorus compounds experimentally, and this not only enables us to find the atomic volumes, but also to give the probable structural formulæ of the different compounds.



Phosphorus trichloride.

$\begin{array}{c} \text{Cl} \\   \\ < \text{P} - \text{Cl} \\   \\ \text{Cl} \end{array}$	$\text{PCl}_3$	$V_m$ 93.3
	P	27.0
	3Cl	66.0
	$\Sigma_n V_a$	93.0
	$V_m$	93.3
		<hr/>

Phosphorus oxychloride.

$\begin{array}{c} \text{Cl} \\   \\ \text{O} = \text{P} - \text{Cl} \\   \\ \text{Cl} \end{array}$	$\text{POCl}_3$	$V_m$ 101.37
	$\text{PCl}_3$	93.0
	O	8.3
	$\Sigma_n V_a$	101.3
	$V_m$	101.4
		<hr/>

Phosphorus sulphochloride.

$\begin{array}{c} \text{Cl} \\   \\ \text{S} = \text{P} - \text{Cl} \\   \\ \text{Cl} \end{array}$	$\text{PSCl}_3$	$V_m$ 116.1
	P	27.0
	$\text{Cl}_3$	66.0
	S	22.0
	$\Sigma_n V_a$	115.0
	$V_m$	116.1
		<hr/>

Phenyl phosphochloride.

$\begin{array}{c} \text{Cl} \\   \\ \text{C}_6\text{H}_5 - \text{P} > \\   \\ \text{Cl} \end{array}$	$\text{C}_6\text{H}_5\text{PCl}_2$	$V_m$ 161.7
	$\text{C}_6\text{H}_5$	92.8
	$\text{PCl}_2$	71.0
		<hr/>
	less for const.	163.8
		- 2.0
		<hr/>
	$\Sigma_n V_a$	161.8
	$V_m$	161.7
		<hr/>

Phosphorus tri-bromide.

$\begin{array}{c} \text{Br} \\   \\ < \text{P} - \text{Br} \\   \\ \text{Br} \end{array}$	$\text{PBr}_3$	
	Bromine appears to have a similar volume to that of phosphorus.	
	$V_m$	108.3
	$\Sigma_n V_a$	108.0 (4 × 27.0)
	I 5 *	

Prideaux has given the volume of  $\text{PCl}_5$  and  $\text{PBr}_5$

Phosphorus pentachloride.

$\text{PCl}_5$	$V_m$ 128.9
$\text{PCl}_5$	128.9
$\text{PCl}_3$	93.3
<hr/>	
2Cl	35.6
Cl	17.8

Phosphorus pentabromide.

$\text{PBr}_5$	$V_m$ 157.3
$\text{PBr}_5$	157.3
$\text{PBr}_3$	108.3
<hr/>	
2Br	49.0
Br	24.5

The usual volumes of the two atoms in question are

Cl 21.6      and      Br 27.0

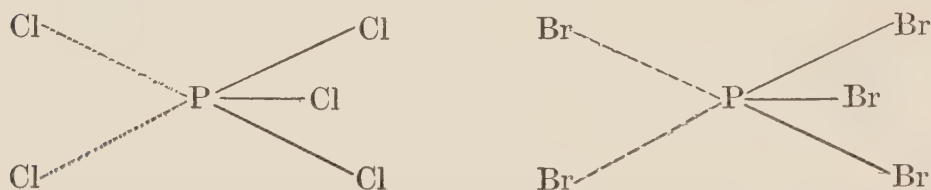
so that there are contractions amounting to

$$\left. \begin{aligned} \Delta_1 &= 17.8 - 21.6 = -3.8 \\ \Delta_2 &= 24.5 - 27.0 = -3.5 \end{aligned} \right\} \text{per additional atom.}$$

These are nearly equal values and they represent total contractions of

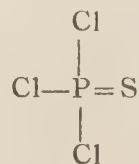
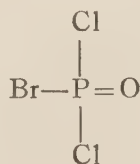
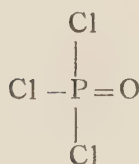
-7.6      and      -7.0 respectively.

If the formulæ of the compounds are respectively



it is difficult to understand why the apparent volumes of the additional atoms should be so small. The obvious conclusion is, that the atoms attached by the two additional valency linkages, possess volumes which are smaller than those attached by the three others, unless some other explanation is available.

Against this view, apparently, are the compounds



from chemical evidence for the volumes of oxygen and sulphur are those which we might expect.

$$O = 8.3$$

$$S = 22.0$$

It follows that in the above respect, the two bromine and chlorine atoms are exceptional, if this be the correct view of the matter. Why this should be so is not evident.

One significant fact is, that although the atoms chlorine and bromine are different in volume, the contractions are about the same.

This might lead us to suppose that the explanation is, that the volume of phosphorus is smaller in these pentavalent compounds than in the trivalent and other pentavalent compounds. We have, however, no good ground for supposing that an atom with its five valencies acting is notably different in volume from that which is true when it only exercises its trivalent function.

For example,

Nitrogen trivalent.



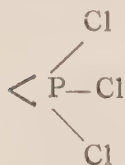
$$V_m \ 31.6 = 2 \times 15.8$$



$$V_m \ 46.8 \quad \Sigma_n V_a \ 46.0$$

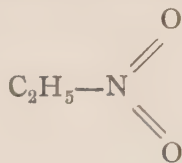
$$N \times 15.6$$

Phosphorus trivalent.

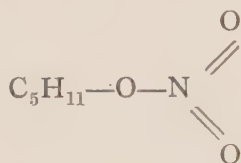


$$V_m \ 93.3 \quad \Sigma_n V_a \ 93.3 \\ P \ 27.0$$

Nitrogen pentavalent.

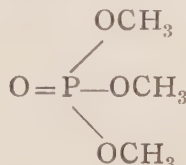


$$V_m \ 80.4 \quad \Sigma_n V_a \ 80.2 \\ N \ 15.6$$



$$V_m \ 152.9 \quad \Sigma_n V_a \ 153.5 \\ N \ 15.6 \quad O' \ 7.4$$

Phosphorus pentavalent.



$$V_m \ 139.7 \quad \Sigma_n V_a \ 138.2 \\ P \ 27.0 \quad O \ 8.3$$

Similar relations have been made out for sulphur, and it has been shown that  $S$ ,  $S^{iv}$ , and  $S^{vi}$  have precisely the same volume.

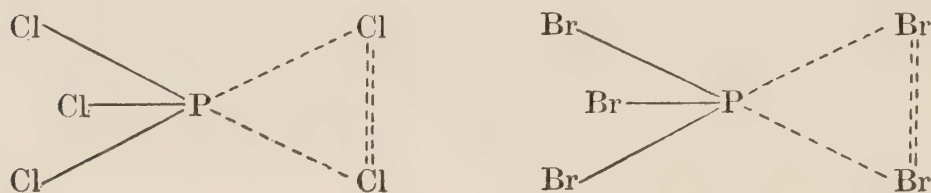
The conclusion is that the volume of pentavalent nitrogen

and phosphorus possess similar volumes to the trivalent atoms. The contractions for  $\text{PCl}_5$  and  $\text{PBr}_5$  are thus not caused by the pentavalency of phosphorus.

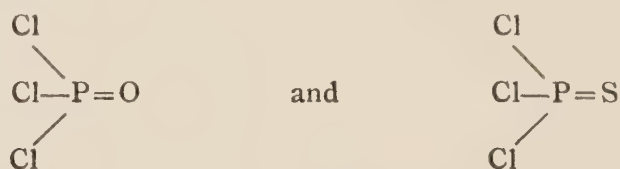
The diminution in volume is thus due to the two additional chlorine and bromine atoms.

It may be supposed that the compounds  $\text{PCl}_5$  and  $\text{PBr}_5$  involve ring structure, the latent valencies of the two additional atoms becoming active.

Thus the constitutive formulæ of  $\text{PCl}_5$  and  $\text{PBr}_5$  might be



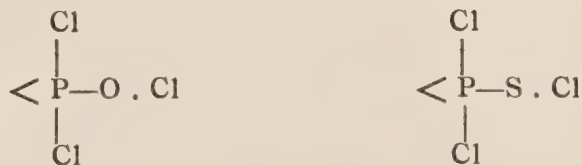
This would also explain why there should be a contraction in the above instances, and not in the case of



The contractions  $-7.3$  (mean) are not inconsistent with this supposition, since  $\Delta_g = -6.5$ .

The only remaining explanation apparently is that phosphorus in its action on the halogens, operates differently in the case of the additional atoms, than on the three ordinary ones. There are however no adequate reasons for this, that is from the stand-point of molecular volumes.

Thorpe, in his discussion of the series of compounds already mentioned, supposed that phosphorus was invariably trivalent, and that the constitutions were

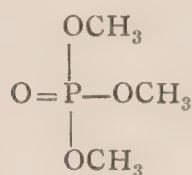


We have seen that this is not the case, viz. that phosphorus is pentavalent. The constitutional formulæ are those which have been given.



Only one or two more compounds remain for investigation. They are

Trimethyl orthophosphate.

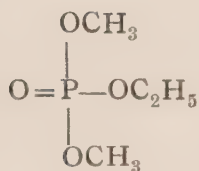


$$V_m \ 139.7$$

$$\begin{array}{rcl} \text{P} & 27.0 & \\ \text{O}'' & 8.3 & \\ 3\text{O}' & 103.0 & (3 \times 8.3) \end{array}$$

$$\begin{array}{rcl} \Sigma_n V_a & 138.3 & \\ V_m & 139.7 & \end{array}$$

Dimethyl ethyl orthophosphate.



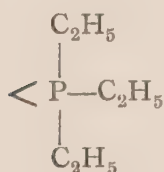
$$V_m \ 161.8$$

Comparing the above two compounds we see that

$$\text{CH}_2 = 22.1$$

its normal value.

Triethyl phosphine.



$$d \ 0.812 \quad \text{b.p. } 127.5 \quad C \ 0.55$$

$$\text{P} \quad 27.0$$

$$V_m \ 170.8$$

$$3\text{C}_2\text{H}_5 \quad 144.0$$

$$\Sigma_n V_a \quad 171.0$$

$$V_m \quad 170.8$$

The value of C was calculated from the preceding compound. No data for ring compounds including phosphorus are available. In all the compounds studied the atomic volume of phosphorus is the same.

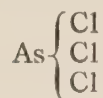
$$\text{P} \ 27.0$$

We have thus found the following atomic values

$$\begin{array}{rcl} \text{N} & 15.6 & \text{N (aminic)} \quad 12 \text{ and over} \\ \text{P} & 27.0 & \end{array}$$

There yet remain the following triatomic atoms to be considered—

## Arsenic As

Arsenious chloride  $\text{As Cl}_3$  $V_m$  94.4 (Thorpe).

As	27.8
3Cl	66.3
<hr/>	
$\Sigma_n V_a$	94.1
$V_m$	94.4
<hr/>	

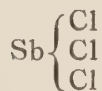
Arsenious fluoride.  $\text{As F}_3$  $V_m$  53.8 (Thorpe).

As	27.8
3F	26.1 (3 × 8.7)
<hr/>	
$\Sigma_n V_a$	53.9
$V_m$	53.8
<hr/>	

Arsenic possesses a volume of only 27.8 in the above compounds.

What its normal value is we cannot say, probably about 30.5.

## Antimony Sb

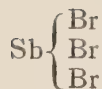


## Antimony trichloride.

 $\text{SbCl}_3$   $V_m$  100.7 (Pierre).

Sb	34.2
$\text{Cl}_3$	66.6
<hr/>	
$\Sigma_n V_a$	100.8
$V_m$	100.7
<hr/>	

## Antimony tribromide.

 $\text{SbBr}_3$ 

Sb	34.2
3Br	82.5 (3 × 27.5)
<hr/>	
$\Sigma_n V_a$	116.7
$V_m$	116.8
<hr/>	

The atoms of this group thus possess the following atomic volumes.

## ATOMIC VOLUMES OF GROUP 5.

Nitrogen (N)	15.6	} $\Delta$
Phosphorus (P)	27.0	
<hr/>		
Arsenic (As)	27.8	} $7.2 = 2 \times 3.6$
Antimony (Sb)	34.2	

# Elements of Group 4.

## Carbon C.

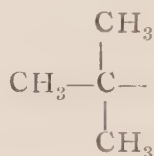
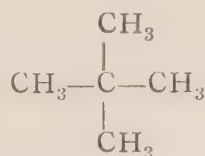
The question of the atomic volume of carbon has been exhaustively treated.

It has always been found that the volume of carbon is

$$C \ 14.8$$

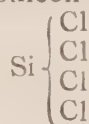
at the boiling-point, or a similar one.

If the additive rule were strictly followed, it would no doubt be shown that carbon has a smaller volume in such compounds or groups as



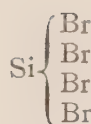
than is usually the case, but we prefer to consider any differences of this nature as being due to constitutive influences possibly affecting the whole molecule.

Silicon Si.



Silicon tetrachloride.

SiCl <sub>4</sub>	V <sub>m</sub> 120.8
Si	32.0
4Cl	88.8
$\Sigma_n V_a$	120.8
V <sub>m</sub>	120.8



Silicon tetrabromide.

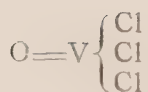
SiBr <sub>4</sub>	V <sub>m</sub> 144.3
Si	32.0
Br	112.0 (4 × 28.0)
$\Sigma_n V_a$	144.0
V <sub>m</sub>	144.3

Vanadium V.



Vanadium tetrachloride.

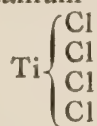
VCl <sub>4</sub>	b.p. 154°	C 0.48
d <sub>0</sub> 1.8584	V <sub>m</sub> 120.8	
V	32.0	
4Cl	88.8	
$\Sigma_n V_a$	120.8	
V <sub>m</sub>	120.8	



Vanadium oxychloride.

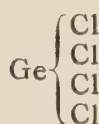
VOCl <sub>3</sub>	V <sub>m</sub> 106.3
V'	32.0
O''	8.3
4Cl	66.6
$\Sigma_n V_a$	106.9
V <sub>m</sub>	106.3

## Titanium Ti



## Titanium tetrachloride.

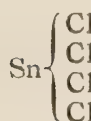
$\text{TiCl}_4$	
$V_m$	124.47
Ti	35.7
4Cl	88.8
<hr/>	
$\Sigma n V_a$	124.5
$V_m$	124.5
<hr/>	

Germanium $\frac{7}{2}$ Ge

## Germanium tetrachloride.

$\text{GeCl}_4$	
b.p. 86.0	$d_{18} \ 1.887 \quad C \ 0.48$
$V_m$	123.3
Ge	34.5
4Cl	88.8
<hr/>	
$\Sigma n V_a$	123.3
$V_m$	123.3
<hr/>	

## Tin Sn



## Tin tetrachloride.

$\text{SnCl}_4$	
$V_m$	131.1
Sn	42.3
4Cl	88.8
<hr/>	
$\Sigma n V_a$	131.1
$V_m$	131.1
<hr/>	

## Elements of Group 4.

	M.W.	$V_m$ .
Carbon (C)	11.0	14.8
Silicon (Si)	28.0	32.0
Titanium (Ti)	48.0	35.7
Germanium (Ge)	72.3	34.9
<hr/>		
Tin (Sn)	118.0	42.3

## Miscellaneous Elements.

Compound.	$V_m$ less $n V_a$ .	
$\text{BoBr}_3$	102.9 - 3 $\times$ 27.5	Bo 20.4
$\text{BoCl}_3$	87.0 - 3 $\times$ 22.0	21.0
		Mean 20.7
$\text{Zn}(\text{CH}_3)_2$	72.0 - 2 $\times$ 26.0	Zn 20.0
$\text{Zn}(\text{C}_2\text{H}_5)_2$	116.7 - 2 $\times$ 48.0	20.7
		Mean 20.4

NOTE.—It will be noted that the atomic volumes of the elements in Group 4 can be arranged on a regular curve (see Fig. 9, p. 236). The same applies to the elements of the other groups. Some are notably out of place. For example As should have an atomic volume of 33 instead of 27 which it is found to possess, and which is similar to the volumes of Se and Br. I with a volume of 37 is also out of place, and should possess one of 32. It thus appears that certain unknown disturbing influences exist which may cause the atomic volumes to be modified. An attempt has been made by a study of organo-metallic derivatives to solve this difficulty. Whilst in certain cases the expected values have been found, in others the disturbing influences are again apparent. As has been found to possess in some compounds its true volume. It is at present impossible to arrive at any definite conclusion till all such compounds have been investigated. In spite of these disturbances the periodic relation noted can be traced from a general study of the elements.



## CHAPTER VIII.

### SUMMARY OF THE THEORY OF MOLECULAR VOLUMES.

#### A. The Additive Principle.

THIS feature, which characterizes most physical properties, is very prominent in molecular volumes, although not, as Kopp thought, unqualified. This being so, it is essential that accurate atomic volumes should be found, at least in so far as this can be done with a property in which the influence of the homologous increment is felt even from compound to compound in a series. The numbers determined by Kopp were, for the most part, inaccurate, chiefly because the values for the fundamental atoms carbon and hydrogen were altogether wrong.

The values which have been found for the various elements in this treatise have been shown to be true, and it is believed that they are so, for the reason that by their use many constitutive effects have been revealed and a fairly consistent theory built up. As regards the series of values, we have come to the same conclusion as Thorpe, even though he utilized Kopp's system in his investigations, that there is a periodic relation to be traced between them. This periodic relation has been more clearly shown by means of the new theory. The characteristic volumes of most of the metals cannot be ascertained at present, but those of the greater number of the non-metals have been calculated. The following table shows the periodic relation indicated:—

THE PERIODIC RELATIONS BETWEEN THE ATOMIC VOLUMES AND ATOMIC WEIGHTS RESPECTIVELY.

Groups.						
1.	2.	3.	4.	5.	6.	7.
H	—	—	—	—	—	—
MW. 1	—	—	—	—	—	—
V <sub>a</sub> 3·7	—	—	—	—	—	—

I.	Li. 7 —	Be. 9 —	Bo. 11 20.5	C. 12 14.8	N. 14 12.0 } 15.6 }	O. 16 7.4 } 12.0 }	F. 19 8.7
II.	Na. 23 —	Mg. 24.3 —	Al. 27 —	Si. 28.3 32.0	P. 31 27	S. 32 21.6 } 25.6 }	Cl. 35.5 22.1
III.	K. 39.0 —	Ca. 40.0 —	Sc. 44 —	Ti. 48.0 35.7	V. 51 32.0	Cr. 52.5 27.4	Mn. 54.8 —
	Cu. 63.2 —	Zn. 65 20	Ga. 70 —	Ge. 72 35.1	As. 75 27	Se. 79 27	Br. 80 27.8.5
IV.	— Ag. 107.7 — —	— Cd. 111.7 — —	— Tn. 113.6 — —	— Sn. 118.8 42.0 —	— Sb. 119.6 [34.3] —	— Ti. 125 — —	— I. 126.5 37.0 —
	V.	Au. 196.7 —	Hg. 200 19.0	Tl. 203.7 —	Pb. 206.4 46.5 } 50.1 }	Bi. 207.3 48.0	— — —

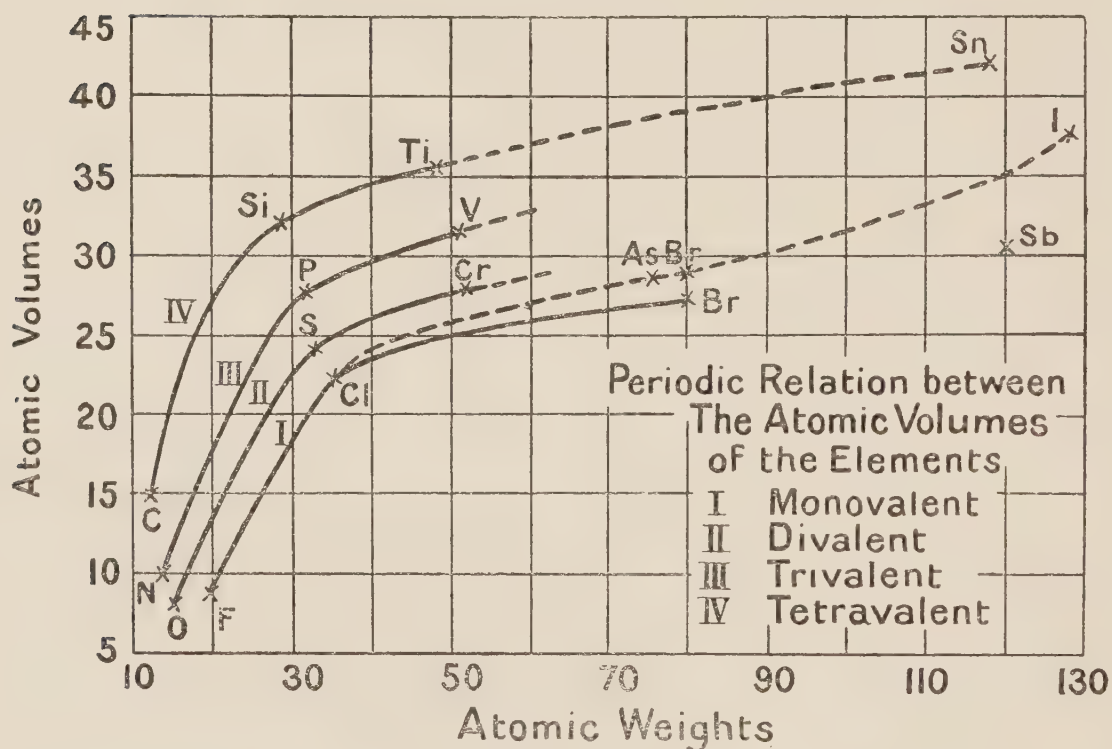


FIG. 9.

In the following table and diagram we include all the information regarding the atomic volumes of the elements and their relations with each other, which has been obtained by means of a study of the molecular volumes of chemical compounds.

We see

(a) *That there is a periodic relation between the atomic volumes of the elements.*

(b) *There is a tendency for the atomic volumes to diminish in each series as the atoms increase in weight. The smallest occur at group seven.*

(c) *There is a general increase in the atomic volumes of the members of each group from series one onwards, that is, in the direction of increasing atomic weight. This increase is usually 3.6 or some multiple thereof.*

### Variations in the Volumes of the Atoms.

This important subject has already been dealt with but we here give a summary of the results arrived at. In considering the variations in the atomic volumes we must distinguish between the general causes of variation involved when the homologous increment  $\text{CH}_2$  is added, and those special influences which affect the volumes of individual atoms or, at least, groups of atoms. It is difficult to separate them.

*Carbon and Hydrogen.*—These atoms do not vary in volume except by reason of increase in complexity when the homologous increment  $\text{CH}_2$  is added. For this reason they vary in each homologous series, and also if we compare the volumes of hydrogen in corresponding members of different series we also find differences

	H
$\text{C}_5\text{H}_{12}$	3.681
$\text{C}_4\text{H}_9\text{I}$	3.671
$\text{C}_5\text{H}_{10}\text{O}_2$	3.647

These differences may be considered to be due respectively to the influence of the typical atoms or groups in each series

—H, —I, —COO— and so on.

The latter are influenced by the complexity of the compounds as well as those of the hydrocarbon chain generally.

In practice it is unnecessary to consider small variations of this character, except in special cases. Thus carbon and hydrogen give the average values of

$$\text{C} = 14.8 \quad \text{H} = 3.70.$$

and these values may be used for all ordinary compounds.

*Oxygen O.*

The element is difficult to deal with since it varies to a considerable extent owing to special constitutive influences, and shows so many different values.

The influence of H and CH<sub>3</sub> is such, that, when in combination with oxygen, the volume of O is reduced to perhaps its smallest value.

*The various volumes of oxygen.*

	Alkyl.	Aromatic.	
O' {	in the OH group (alcohols and phenols)	6.4	5.6
	in the ethers— "    "    (acids)	7.4	
	—OCH <sub>3</sub> group	9.1	7.6
	—OR	9.5-11.0	10-11
	in the esters	7.4	
O'' {	doubly bound oxygen O''—		
	in the aldehydes and ketones	7.4	
	in the acids	12.0	
	in combination with P, S, and N	8.3- 9.2	
>O	ring oxygen (as in ethereal compounds).	7.4-11.0	

*Sulphur S.*

There are two values for this element

(a) S 25.6      (b) 21.6-22.5.

The first is found in the mercaptans and the thio-ethers, also in those which show differences among themselves in the valency values of sulphur: —S— as in Cl—S—Cl, in the mercaptans R—S—H and thio-ethers R—S—R', also in a few inorganic

compounds with =S= and  $\begin{array}{c} | \\ =S= \\ | \end{array}$ .

(b) The second value is found in the following groups: —S—C≡N; —N=C=S, also in S=C=S, and ring sulphur. No other value for =S is found.

*Nitrogen N.*

There are two characteristic types of nitrogen:—

(a) 15.6 for N≡N, and in a few simpler compounds like NH<sub>3</sub>, NCl<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>4</sub>, and in the groups



also possibly in others.



## (b) Amino nitrogen

in the primary amines with the group—NH<sub>2</sub>, 10.5  
 in the secondary amines—NHR— and —NR<sub>2</sub>, 12.0

It has been hitherto supposed that only polyvalent elements vary in volume, but we shall see that probably others also do so.

*Chlorine Cl.*

Terminal chlorine Cl'	21.6
Medial chlorine Cl''	24.6
R—Cl'	R—CHCl''—R'

A number of intermediate values are found.

When attached to the nucleus of benzene two distinct values for chlorine are known, 19.0 and 21.6.

**B. Constitutive Influences.**

The physical property of molecular volumes is marked to a considerable extent by the influence of constitution. The chief influences which have been worked out in this volume will be briefly described here.

*(a) The Influence of the Homologous Increment.*

An exact study of the mode of variation of the volumes of the atoms in a number of series may be made by utilizing the following principle:—

*The relative volumes of the atoms remain the same in the different members of a homologous series, although their actual volumes differ from one another.*

This has enabled us by means of the relation

$$V_m = WS$$

where W is the number of hydrogen equivalents, to find S the volume of hydrogen or its equivalent.

The series of values so found for any homologous series, may be represented by *curves* which show the variation of the atomic volumes throughout the series.

By this means, we have been able to show that the volumes of the atoms of the first two or three compounds in each series, and, therefore, those of the compounds, are relatively large. The values decrease to a minimum at about the fifth member in each series and then increase in the remaining compounds.

These *curves* cannot be exactly represented by any formula,

but utilizing the fact that the mode of variation after the fifth member is nearly rectilinear, we may utilize the following formula to calculate the volumes of the compounds in a series:—

$$V_m = W \{S + (W - N)K\}$$

W being the number of hydrogen equivalents of a compound.

S the volume of hydrogen which is least in a series.

N the number of hydrogen equivalents in the corresponding compound.

K the increment in the volume of hydrogen or its equivalent when hydrogen or its equivalent is added to a compound.

For particular series the formulæ are:—

For the normal paraffin series  $C_nH_{2n+2}$ ,

$$V_m = (6n + 2) \{3.681 + (6n - 36) \times 0.0045\}.$$

For the formic ester series  $H \cdot COOR$ ,

$$V_m = (6n + 7) \{3.647 + (6n - 28) \times 0.00375\}.$$

For the alkyl iodide series  $C_nH_{2n+1}I$ ,

$$V_m = (6n + 11) \{3.671 + (6n - 24) \times 0.00433\}.$$

$n$  is the number of carbon atoms in a compound.

$$C = 4H, O' = 2H, O'' = 3H, Cl = 6H, Br = 7.6H, I = 10H.$$

The method may be useful to calculate the volume of a compound high in any particular series.

Thus, if we require to find the molecular volume of say heptyl iodide  $C_nH_{2n+1}I$ , we find by use of formula 3 shown above the following result.

$$V_m \text{ (calc.) } 198.7 \qquad V_m \text{ (obs.) } 198.6$$

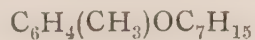
The method may be useful in cases which have not been investigated experimentally—

as e.g.  $n$  decane  $C_{10}H_{22}$

$$V_m \text{ (calc.) } 234.8 \qquad V_m \text{ (by form.) } 234.9$$

using formula 1 above.

In the aromatic series of the phenolic, cresylic, and other ethers, the benzoates and other series, it is found that the addition of the homologous increment  $CH_2$  beyond the third, attached to the nucleus involves a total increase in volume of 3.7 per  $CH_2$  increase.

*p* Cresylic heptyl oxide.

$$V_m \ 298.3$$

$\text{C}_6\text{H}_4$	89.6
$\text{CH}_3$	25.5
$\text{O}$	5.6
$\text{C}_7\text{H}_{15}$	159.1
	<hr/>
	279.8
$(\text{C}_8-\text{C}_3)$	18.5 (5 × 3.7)
	<hr/>
$\Sigma_n V_a$	298.3
$V_m$	298.3
	<hr/> <hr/>

Unfortunately very few series have been examined with that degree of accuracy which would make the method generally useful, but sufficient evidence has been given to show us that we can extend the scope of our inquiries to fairly complex compounds, if we possess the requisite material for calculation.

(*b*) *The Influence of Unsaturation.*

(i) It is a remarkable fact that, for the most part, unsaturation produces no apparent effect on the molecular volumes of compounds, other than that which is occasioned by the subtraction of atoms. It is true that saturated and unsaturated compounds differ in volume by about that amount which is due to their difference in composition. This difference in composition, as a rule, is two or four atoms of hydrogen.

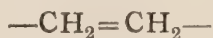
UNSATURATED COMPOUNDS.

Compounds.	$V_m$ .	$\Delta V_m$ .	b.p.
$\text{C}_5\text{H}_{12}$	117.8		38.0
$\text{C}_5\text{H}_{10} \equiv $	110.1	7.7	39.0
		2 × 7.0 (app.)	
$\text{C}_5\text{H}_8 \equiv _2$	103.9		
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_3$	139.3		136.5
		7.9	
$\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH}_2$	131.4		146.2
		2 × 6.55	
$\text{C}_6\text{H}_5 \cdot \text{C} : \text{CH}$	126.2		141.6
$\text{C}_3\text{H}_7\text{OH}$	81.4		97.1
		7.3	
$\text{C}_3\text{H}_5\text{OH}$	74.1		94.4
$\text{C}_3\text{H}_7\text{Cl}$	91.9		46.0
		6.9	
$\text{C}_3\text{H}_5\text{Cl}$	85.0		46.0
$\text{N}(\text{C}_3\text{H}_7)_3$	222.5		—
		3 × 7.2	
$\text{N}(\text{C}_3\text{H}_5)_3$	200.7		—
	16		

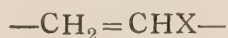
The average volume of hydrogen in both saturated and unsaturated compounds is about 3·7 and  $H_2 = 7\cdot4$ . This is seen from the foregoing table:—

Comparatively few unsaturated compounds are available for study, but there seems to be some disturbance, when an unsaturated atom or group is in association with a  $|=|$  or  $|\equiv|$  link.

We have just studied the group



(ii) When, however, the group is



where X is such unsaturated atom or group there is generally an increase in volume. For example,

Ethylene bromide  $\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$

$V_m$  97·7

Acetylene dibromide  $\text{CHBr} : \text{CHBr}$

$V_m$  92·3

$\Delta$  for  $H_2$  5·4      Now  $H_2$  equals 7·3.

The relative increase is therefore

+ 1·9

This can be otherwise calculated

$\text{C}_2\text{H}_4\text{Br}_2$		$\text{C}_2\text{H}_2\text{Br}_2$	
$\text{C}_2\text{H}_4$	43·2 (2 × 21·6)	$\text{C}_2\text{H}_2$	36·0
2Br	54·4 (2 × 27·2)	2Br	54·4
$\Sigma_n V_a$	97·6	$\Sigma_n V_a$	90·4
$V_m$	97·7	$V_m$	92·3
		$\Delta$	+ 1·9

Acetylene tetrachloride.



b.p. 147·0       $d_0$  1·614      C 0·45

$V_m$  120·5

or  $\text{CCl}_3 \cdot \text{CHCl}_2$       138·2 (Thorpe)  
less Cl      - 21·6

plus H      116·6  
+ 3·7

$\Sigma_n V_a$       120·3  
 $V_m$       120·5



Tetrachlorethylene.



$V_m \ 114.8$

$\Delta \text{ for H}_2 \ 5.7 \qquad \text{H}_2 \ 7.3$

$\text{Increase} + 1.3$

The augmentation is not due to the chlorine atoms directly, since it is not affected by their number. We must consequently ascribe it to the ethenoid linkage  $|\equiv|$

Tribrom methane.

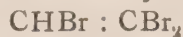


$V_m \ 119.3$

 $\Delta$ 

$5.7$

Tribrom methylene.

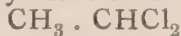


$V_m \ 113.6$

The above cases involve a halogen atom on both sides of the ethenoid link  $|\equiv|$ , and in such circumstances the apparent influence of these halogen atoms thereon seems indubitable.

Cases occur in which a halogen atom only is found, and the evidence is here somewhat contradictory.

Ethylidene chloride.



$V_m \ 88.9 \text{ (by obs.)}$

$89.0 \text{ (by form.)}$

$\Delta \ 8.9$

$C = 0.46$

$7.2 \text{ for H}_2 \text{ and } \Delta - 1.7.$

Unsymm. dichlorethylene.



$V_m \ 79.9 \text{ (by obs.)}$

$80.1 \text{ (by form.)}$

In this case the volume of  $\text{CH}_2 = \text{CCl}_2$  is diminished instead of increased by the amount 1.7, but there is apparently some disturbing influence.

It will have been noticed that in the compound  $\text{CCl}_2 : \text{CCl}_2$ , the value of  $\Delta$  is + 1.3, which thus shows a relative expansion as compared with the saturated compound.

In the case of the bromine compound, the result is different—



$99.8$

$6.8$

$\Delta + 1.4$



$93.0$



$77.1$

$5.8$

$\Delta + 1.4$



$71.3$

In calculating the values for derivatives of ethane, it is necessary to use considerably larger atomic values, than for propyl derivatives. This complicates matters. The reason is, that as we pass from methyl ( $\text{CH}_3$ ), ethyl ( $\text{C}_2\text{H}_5$ ), and propyl ( $\text{C}_3\text{H}_7$ ) derivatives, the change in volume for the addition of  $\text{CH}_2$  is usually considerable. It follows that the volume of hydrogen will largely depend upon what atom or group is the substituent of ethane. The volume of hydrogen for the bromine compounds under consideration is about 3.8.

(iii) It is probable that there is also some volume disturbance in the groups



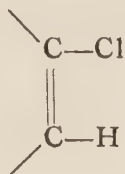
due to the presence of the methyl group.

The effect of other groups, if any, is not known at present.

(iv) It has been shown that in the aromatic halogen compounds the volumes are similar to those in paraffinoid derivatives.

$\text{C}_6\text{H}_5\text{Cl}$	$V_m$	114.6	Cl	21.8	Cl (paraff.)	21.6
$\text{C}_6\text{H}_5\text{Br}$	$V_m$	120.0	Br	27.2	Br	27.0
$\text{C}_6\text{H}_5\text{I}$	$V_m$	130.7	I	37.9	I	37.0

Most of the other unsaturated atoms and groups show a diminution when attached to the radical  $\text{C}_6\text{H}_5$ . Halogen compounds apparently do not. If however we suppose that in the group



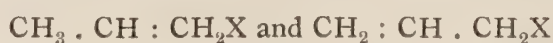
the usual diminution of  $-1.5$ , due to the combination of chlorine with the  $\text{C}_6\text{H}_5$  group, be neutralized by the augmentation  $+1.5$ , caused by association of chlorine with the  $||$ , we have a possible explanation of the exceptions to the rule just noticed.

We notice that the apparent volume of iodine is considerably larger in  $\text{C}_6\text{H}_5\text{I}$  (as in allyl and propargyl iodides) than in saturated derivatives.

The effect of the increasing magnitude of the substituent is seen in the compounds just mentioned.

Propyl compounds.	$V_m$ .	$\Delta$ .	$V_m$ .	Allyl compounds.
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	91.4	7.2	84.2	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{Cl}$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$	97.4	6.9	90.5	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{Br}$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$	106.9	5.7	101.2	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{I}$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOCH}_3$	104.2	5.8	98.4	$\text{CH}_2 : \text{CH} \cdot \text{COOCH}_3$
				Propargyl compounds.
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$	92.0	14.3	77.7	$\text{CH} : \text{C} \cdot \text{CH}_2\text{Cl}$
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{I}$	107.1	12.5	94.6	$\text{CH} : \text{C} \cdot \text{CH}_2\text{I}$

A thorough investigation of all these phenomena would enable us to solve many problems of constitution, such as, for instance, differentiation between compounds of the types

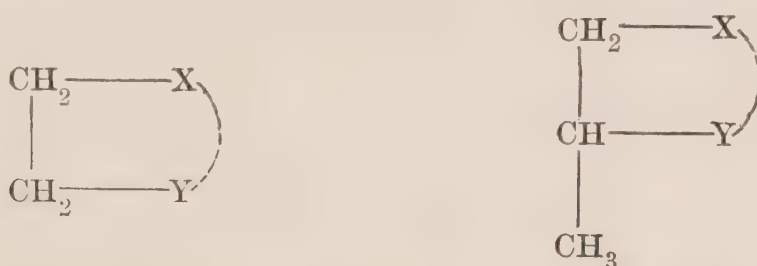


*(c) Partial Ring Structure.*

Intermediate between open and closed chain compounds are what are known as

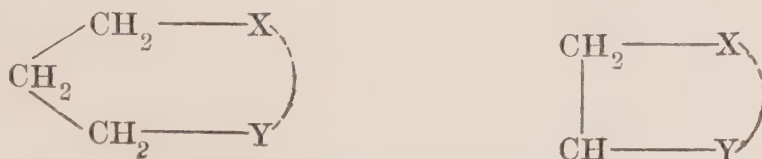
**Partial or Incomplete Rings.**

In order that they may be formed, it is necessary that two atoms or groups, which may be supposed to possess residual affinity, occur in a hydrocarbon chain attached to different carbon atoms. If the carbons are near to each other, there is no need to suppose any variation from structure usually considered when the tetrahedral arrangement of the valency links of carbon is understood. The additional feature of curvature of the hydrocarbon chain may also be the normal condition of things. In the case of saturated compounds the plane formulæ are figured thus —

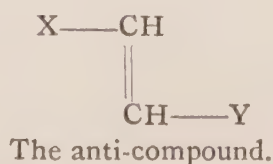
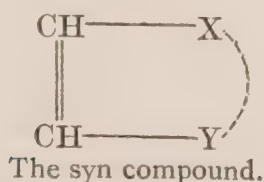


If the two attracting groups are united to carbons not in the immediate neighbourhood of each other, we must suppose that they are brought near by the curvature of the hydrocarbon chain, or the alternative supposition just given is true. In any case such a structure affects the molecular volumes of compounds.

Thus—



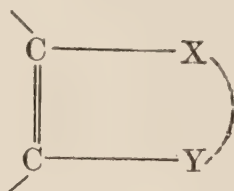
If the compound be unsaturated, it is necessary to suppose two forms which may thus be represented—



The former would be smaller in volume.



We must also suppose that in the benzene di-substituted molecule the ortho form would be



This, however, according to the tetrahedral arrangement of the carbon links, could be given two types of arrangement: one in which the atoms or groups appeared on the same side of the ring and one in which they would be disposed on the opposite sides.

It should be remarked that in the saturated chain there is no hindrance to the two reactive groups occupying the sign position, so that only one form is possible. In the unsaturated chain the possible rotation about an axis joining two carbon atoms is prevented by the residual affinity associated with an ethenoid link. Two forms are thus possible.

The attracting atoms or groups are the halogen atoms Cl, Br, I, the hydroxyl group OH, the amino  $\text{NH}_2$ , etc., the nitro  $\text{NO}_2$ , the carboxyl  $\text{COOH}$ , and perhaps other groups.

The contraction

for  $\alpha\beta$  compounds is about  $-3.0$   
 „  $\alpha\gamma$  „ „  $-4.5$

In ring-compounds the ortho arrangement has been specially studied (q.v.).

#### (d) Ring Structure.

This subject has already been dealt with at some length, but the chief points can here be stated.

Ring compounds are invariably characterized by contractions. This is due to a diminution in the individual atomic volumes forming the nucleus, and also in the case of the associated hydrogen atoms, when such are present.

The compounds (a) *benzene* and (b) *hexamethylene* have been studied not only at the critical and boiling-points but also at corresponding pressures, and it has been shown that *the relative volumes of the atoms remain the same as in straight-chain compounds*.



The contractions for single-ringed compounds are

$$\square_3 - 6.5 \quad \square_4 - 8.5 \quad \square_5 - 11.5 \quad \square_6 - 15.0 \quad \square_7 - 20.0 \quad \square_8 - 25.5$$

Double and triple rings have contractions

$$\begin{array}{l} \boxed{\square} \text{ }_{6+5} - 26.0 \quad \boxed{\square} \text{ }_{2 \times 6} - 30.0 \text{ camphor, etc. } - 31.0 \\ \boxed{\square \square} \text{ }_{3 \times 6} - 48.0 \quad \boxed{\square \square} \text{ }_{2 \times 6+5} - 45.0 \end{array}$$

Not many independent double-ring compounds are available for study.

(e) *Molecular Volume and Valency.*

It has been supposed that there is a connection between volume and valency. However this may be in a general sense, there is no clear connection between the volume and the fundamental valency. When, however, we compare the atomic volumes in the different series of the periodic arrangement of the elements, we find a general indication of a similar increase from series to series. For example:—

					Averages.
Series I	C 14.8	N 15.6	O 11.0	F 8.7	
$\Delta$	+ 17.2	+ 14.6	+ 11.4	+ 13.4	14.1 = 4 × 3.7
Series II	Si 32.0	P 27.0	S 22.0	Cl 22.0	
			25.6		
			M. 23.8		
$\Delta$	+ 3.7	+ 5.0	+ 3.6	+ 4.9	4.3 = 1 × 4.3
Series III	Ti 35.7	V 32.0	Cr 27.4	Br 27.0	
	Ge 35.1	As 27.0	—	Br 27.0	
$\Delta$	+ 6.9	+ 7.3		+ 10.0	8.0 = 2 × 4.0
	Sn 42.0	34.3	—	I 37.0	

These differences vary somewhat, but they are similar. It is, however, probable that the numbers themselves, which vary considerably under different circumstances and with various environments, are not quite the significant volumes. In order to arrive at a generalization of more than qualitative significance, it is necessary to know precisely what the term molecular volume stands for and it is also necessary that the atoms should be placed under comparable conditions. How much of the real molecular volume space consists of atoms with their shells, and how much is made up of their movements of vibration we do not know. It is possible that some simple relation between volume and valency, similar to that discovered by Barlow and Pope, might be discovered if we could divide up the apparent volumes into their real parts. This may one day be possible, and the relation, one of simple proportionality, discovered,

The unit 3·7 seems to be significant for (a) several atoms are integral multiples of this unit—

$$\text{C } 14\cdot8 = 4\text{S} \quad \text{H} = 3\cdot7 = \text{S} \quad \text{O} = 11\cdot0 = 3\text{S} \quad \text{S} = 25\cdot6 = 7\text{S}.$$

Also (b) several atoms of varying atomic volume seem to show volumes which differ by just this unit—

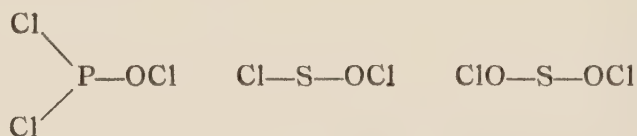
O	7·4	S	22·0	N	12·0
	11·0		25·6		15·6
	<hr/>		<hr/>		<hr/>
	3·6		3·6		3·6
	<hr/>		<hr/>		<hr/>

The possibility of variation in the atomic volumes corresponding to variations in acting valency thus occurs.

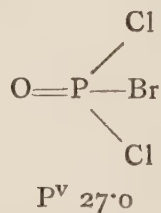
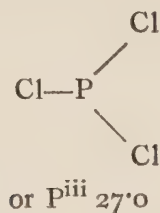
It has been thought that as the acting valency of an atom changes its volume varies also. This is found not to be the case.

Thorpe has stated this in the course of his work on molecular volumes. Thus: "The inquiry affords us no evidence in favour of the hypothesis that the specific volume of an element in combination is modified by any possible variation in the affinity value which it may possess. The observation of compounds of sulphur and phosphorus appear conclusive on this point."

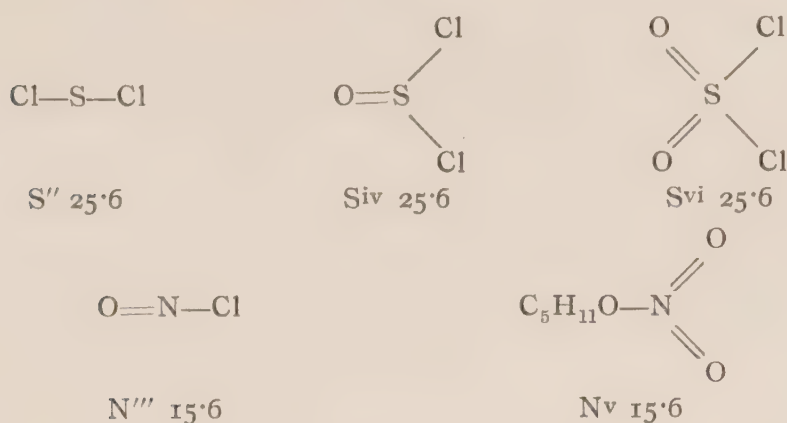
We do not know how Thorpe came to this conclusion, since his formulæ make phosphorus trivalent and sulphur divalent—



With the accepted formulæ, which are confirmed by means of our theory, we find that phosphorus and sulphur may act with varying valencies. There is, however, no change in the atomic volumes of the elements due to this cause, as Thorpe supposed.



\* It should be mentioned that Prideaux' values for PCl<sub>5</sub> and PBr<sub>5</sub> seem to lead to a different conclusion, but his observations are capable of another explanation (q.v.), and in any case are exceptional.



We do not possess the requisite data for any other elements, but the results just obtained appear conclusive on this matter.

It is true that the volumes of the elements vary, but this variation cannot be shown to be due to their variable valency relations, but to some other cause.

$\text{S}''$	21·5 and 25·6
$\text{N}'''$	12            15·6
$\text{O}''$	7·4            11·0
$\text{Br}$	27·0 to 28·5

*(f) The Constitutive Influences Due to Groups.*

The question of special influences due to groups is a very important one, and for thorough treatment many more accurate data are needed than are at present available. In so far as the homologous open-chain series are concerned, the additive rule may, for practical purposes, be said to prevail, unless the complexity be greater than a certain amount.

*Volumes of Groups in Organic Compounds.*

$\text{CH}_3 \ 26\cdot0$	$\text{C}_2\text{H}_5 \ 48\cdot0$	$\text{C}_3\text{H}_7 \ 70\cdot0$	$\text{C}_4\text{H}_9 \ 92\cdot3$	$\text{C}_6\text{H}_5 \ 92\cdot8$
$\text{OH} \ 10\cdot0$	$\text{CHO} \ 25\cdot9$	$\text{CO} \ 22\cdot0$	$\text{COOH} \ 37\cdot8$	
$\text{NH}_2 \ 17\cdot4$	$\text{NO}_2 \ 32\cdot0$	$\text{CN} \ 30\cdot4$	$\text{S} \cdot \text{CN} \ 52\cdot0$	

The volumes are average ones for the groups in question, but they do not vary very much under ordinary circumstances except perhaps for the group  $\text{CH}_3$ . Taking the average volumes of the atoms already indicated, we find how the volumes of the groups  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$  may vary according to the particular typical atom or group to which it is attached. The ethyl  $\text{CH}_3$  group varies most, the  $\text{C}_2\text{H}_5$  group to a lesser extent, and both vary most

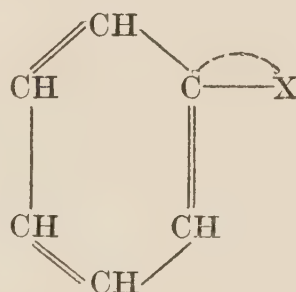
when H, OH and Cl are the other groups making up the compound. These variations are due to causes not quite understood as yet, but probably complexity is one of them.

It is also possible that there may be some interactions between the alkyl and other groups. An important example of variation in the values of the groups is found when they are attached to aromatic radicals like phenyl  $C_6H_5$ . The volume of this group is taken as 92.8, and the volumes of the other groups as in the preceding table.

*The Contractions Found when Unsaturated Groups are in Union with the Phenyl Group  $C_6H_5$ .*

Group.	$\Delta$ .	Group.	$\Delta$ .	Group.	$\Delta$ .
—OH	—0.9	—COOH	—3.9	CH <sub>3</sub> and other alkyl groups } —0.5	
—CN	—1.6	—CH <sub>2</sub> Cl	—1.9		
—NH <sub>2</sub>	—4.3	—NO <sub>2</sub>	—2.7		
—COCl	—1.8	—PCl <sub>2</sub>	—2.0		

These variations may be ascribed to some interaction between the phenyl  $C_6H_5$  radical and the unsaturated groups. For this reason the formulæ, representing this constitutive action, may be shown generally as—



X representing the unsaturated group.

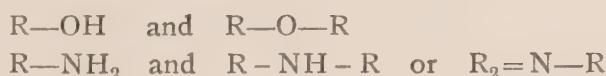
It is easy to show that unsaturation is the cause, because when the hydrogen in the OH and COOH groups are replaced by alkyl groups like CH<sub>3</sub> the contractions disappear.

		$V_m$	$\Sigma_n V_a$	$\Delta$
Phenol	$C_6H_5 \cdot OH$	102.0	102.9	—0.9
Anisol	$C_6H_5 \cdot OCH_3$	125.4	125.2	—
Benzyl alcohol	$C_6H_5 \cdot CH_2OH$	123.7	125.2	—1.5
Anisol	$C_6H_5 \cdot OCH_3$	125.4	125.2	—
Benzoic acid	$C_6H_5 \cdot COOH$	126.9	130.6	—3.7
Ethyl benzoate	$C_6H_5 \cdot COOC_2H_5$	174.4	174.1	—
Phenyl propionic acid	$C_6H_5 \cdot CH_2 \cdot CH_2COOH$	170.9	174.1	—3.2
Ethyl benzoate	$C_6H_5 \cdot COOC_2H_5$	174.4	174.1	—



It has already been shown that the group  $\text{NH}_2$  is responsible for a contraction of  $-4.3$ . It is remarkable that the groups  $-\text{N}(\text{CH}_3)_2$ ,  $-\text{N}(\text{C}_2\text{H}_5)_2$  produce the same contraction, a fact which points to the common atom nitrogen as being the part affected. If the group be unsaturated, e.g.  $\text{N}(\text{C}_3\text{H}_5)_2$ , the contraction is apparently greater.

Not many other groups have been sufficiently studied, but cases which are subject to such contractions may be given. For instance, if we compare



we find that

$$\begin{array}{l} \text{O} = 6.4 \quad \text{and} \quad 10.0 \\ \text{N} = 10.5 \quad \text{and} \quad 12.0 \end{array}$$

Such cases are, however, difficult to adequately account for. This is one of the great difficulties which attend the study of the molecular volumes of open-chain organic compounds, for it is not quite clear whether and to what extent the individual groups making up these compounds influence one another. Such a study is easy in ring compounds such as benzene derivatives, and under such circumstances a fairly complete and reliable analysis has been made.

**C. A discussion of the special conception embodied in molecular volumes, and the relation which obtains between this property and other physical properties such as boiling point, surface tension and viscosity.**

A discussion of the special conception embodied in molecular volumes, and the relation which obtains between this property and other physical properties such as boiling point, surface tension and viscosity.

It is hardly possible in a formal treatise like the present to altogether avoid dealing to some extent with the physical meaning of molecular volumes, and the derived conception of atomic volume.

If the *specific volume*  $= \frac{1}{d}$  in c.c., then the *molecular volume* of say pentane  $C_5H_{12}$  is

$$0.612 \frac{MW}{d} = \frac{72}{0.612} = 117.6$$

at the normal boiling-point.

The molecular volume in the first instance is the volume of that weight which represents the weight of the molecule, or the molecular weight multiplied by the specific volume. This volume under well-defined conditions such as those obtaining at the boiling-point may be supposed to bear to the real molecular volumes, a relation, which is the same for all substances, and thus proportional to the real molecular volumes. This was assumed by Kopp when he started on his investigations of the molecular volumes of liquid organic compounds at the boiling-point, and this has been justified by subsequent work.

It has been shown that

$$\begin{aligned} V_{b.p.} &= \frac{3}{8} V_c \\ \text{but } V_0 &= \frac{1}{4} V_c \\ \therefore V_{b.p.} &= \frac{4}{1} \times \frac{3}{8} V_0 = \frac{3}{2} V_0 \end{aligned}$$

that is, the volumes of the most various liquid compounds are, at the normal boiling-point, one and a half times the volume at absolute zero. This volume  $V_0$  is consequently proportional to the real molecular volume, and so are also the volumes at the boiling-point  $V_{b.p.}$

If the law were strictly followed, the investigation of the molecular volumes of compounds would be a simpler matter than it is. It depends upon the fact that the internal pressures are the same for all compounds at the boiling-point, subject to small variations due to differences in complexity and other causes. These disturbances destroy the simplicity of the rules regulating the relation between the atomic volumes to the whole molecular volume. Young, who investigated a number of organic substances minutely, from the point of view of Van der Waal's equation of condition, attributes the departures from Van der Waal's theory to the constitutive influences.

We have reason to believe that in liquids the molecules exist under an intense intermolecular pressure, which affects the boiling-points of the compounds, their surface tensions, and their viscosities. These intermolecular affinity forces act in such a way as to oppose the heat forces, which consist of vibratory movements

of some kind. The intermolecular forces, presumably of great magnitude, together with the heat forces serve to limit the molecular motions and define the space called the molecular volume. If we consider simply those portions of the molecules called the nuclei, measured by  $\Sigma r_D$ , in the Lorenz-Lorentz formula, or considered in the Clausius theory, it is impossible that they should completely fill the space occupied known as the molecular volume. There must of necessity be a molecular interspace as well as possibly atomic interspaces. This interspace is measured by  $V - b$  according to Van der Waal's formula.

We may now consider the question :—

(a) Of what constitutes the atom and consequently the molecule, and

(b) What is the nature of the molecular movement?

If the Boscovitchian hard atom cannot be entertained, owing to the necessity of accounting for the elastic properties of matter, we must suppose that the nucleus just referred to is enclosed within a shell of dielectric. We consider in the first place that the molecule is made up of the atomic nuclei and its real volume is equal to their sum. The atomic nucleus is however not the whole of the atom, for if we were to cool a substance to absolute zero we should find that it occupied a volume considerably in excess of that of this molecular skeleton so to speak. In other words the term  $b$  of Van der Waal's formula is considerably larger than  $\Sigma r_D$  of the Clausius theory. Traube supposes that,

$$b = 3.5 \text{ or } 4 \Sigma r_D.$$

He employs the molecular refraction as a measure of the nuclear volumes of the atoms contained in a substance, and moreover calculates that the molecular refraction of a saturated compound is proportional to the number of valencies of the component atoms. At any rate this atomic shell represents that portion of the atom which is permeable to light, and constitutes that dielectric medium which enables electro-magnetic radiations generally to traverse the liquid at a speed which is characteristic of the particular liquid under consideration. *The molecular volume at absolute zero is thus equal to the sum of the atomic nuclei plus the sum of the dielectric shells.* It may be supposed that the chemical forces which bind atom to atom to form a molecular combination, is accompanied by stresses and strains in this dielectric.



We are now asked to consider a space equal to one and a half times the volumes of all the atomic nuclei in the molecule:—

$$\text{since } V_{b.p.} = \frac{3}{2} V_0 = \frac{3}{2} b.$$

That this space is occasioned by motion of some kind, is obvious, but on the nature of this motion there has been much dispute. One consideration, which may prove of considerable importance, has never been commented on to the best of our knowledge.

It is this,—why may not the dielectric medium itself expand with rising temperature and fill up the extra space occupied by the liquid caused by the separation of the molecular and also the atomic centres? It is not difficult to imagine such a condition. We may suppose for instance that the dielectric consists of a series of shells of diminishing magnitude as we approach the centre, and related in such a way that a central section would show a spiral originating from the atomic nucleus. Energy could become latent by the “solid spiral” contracting as a watch spring contracts when it is wound up, and moreover could vibrate by a repeated winding and unwinding within limits dependent on the stress within the medium as an ordinary spring might do. Such a motion of the shell, combined with the resultant motion of the nucleus, would constitute the heat motion. We do not insist on this particular mechanism, but give it for what it is worth. The idea of a dielectric expands as the temperature rises, is, however, worthy of every consideration, for we know that the index of refraction  $\mu$ , and therefore the velocity of light in the particular liquid medium, is a function of the temperature. It may be stated that the dielectric shells might not be susceptible to differences in density from compound to compound or for one compound under various conditions, in the same sense that matter in general differs in density. The differences might consist of different degrees or kinds of strain.

If we consider the whole molecule and its expansion under the influence of temperature, we see that there is every reason to suppose that under circumstances of equal internal pressure or under corresponding conditions, the volumes of the molecules should be proportional to their absolute zero volumes and thus of their real molecular volumes. It is however possible, and indeed probable, that as we approach the critical point, certain disturbances might occur which cause departures from ideal conditions, and from the more simple conditions which occur at or near absolute zero.



This, in effect, is the result of the remarkably short range of the affinity forces, and the consequent rapid variation with the distance between the molecular centres. It follows that constitutive features which are apparent at or near the melting point are to some extent marked at and above the boiling point.

### *The Visibility of the Liquid.*

In our view, one circumstance of great significance is, that, when a vapour condenses it becomes *visible*. Steam, for example, condenses to a transparent but visible liquid water, which, except for conditions of mobility, maintains certain characteristics below the melting-point and in the solid state which are noticed in the liquid. The clear limpid water solidifies to the clear glassy ice and this characteristic is maintained down to absolute zero. For that matter an opaque liquid like mercury maintains this characteristic below the melting-point, and so far as we know even to absolute zero. In both cases, however, the vapours are transparent. The reason is, that in the vapours, the light passes through the interspaces which separate the molecules, but in liquids when transparent, it passes through a different medium, the dielectric shells of the atoms and possibly of the molecules as a whole, and this condition is maintained down to absolute zero. We believe that the features just noted can only be explained on the assumption of *compact structure* in the sense indicated. It is also to be remarked that the theory of absorption spectra implies that light traverses a medium different to that of the external ether.

It is not difficult to understand why Richards should have come to the conclusion that the atoms in a liquid as in a solid molecule are in actual contact with each other. We think that, it is necessary to go a step farther and to suppose that the molecules as just defined, are also in actual contact. It is thus found that liquids are compact aggregations of molecules of definite and characteristic compressibility under well-defined conditions, and that the compressibility of the liquid as a whole, measures the compressibility of the dielectric associated with the atomic nuclei. The question of the mobility of the molecules under such circumstances will be referred to immediately.

Another idea of considerable moment, and one derived from a study of molecular volumes, is that if there is considerable motion of translation of the molecules with its consequent impacts, then these motions of translation will depend upon the molecular

weights. We should thus expect that a heavy molecule like  $C_{16}H_{34}$ , would slow down as compared with a light one like butane ( $C_4H_{10}$ ) or pentane ( $C_5H_{12}$ ).

According to the kinetic theory

$$\text{pressure } p = MNV^2$$

M representing molecular weight, N the number of molecules, V the velocity.

If we compare two molecules of different complexities then for 1 gr. mol. of each substance

$$\frac{p_1}{p_2} = \frac{M_1 V_1^2}{M_2 V_2^2}$$

Since at the boiling-point  $p_1 = p_2$

$$\frac{M_1}{M_2} = \frac{V_2^2}{V_1^2} \text{ or } (\text{velocity})^2 \propto \frac{1}{\text{molecular weight}}$$

Thus a small molecule like  $C_5H_{12}$  might be expected to occupy a large volume as compared with a heavy one like  $C_{16}H_{34}$ .

We find that the opposite is the case. Pentane  $C_5H_{12}$  at the *boiling-point* occupies a volume of 117.8. A similar complex in octane  $C_8H_{18}$  occupies a volume of

$$\begin{aligned} &32 \times 3.725 \\ &= 119.2 \end{aligned}$$

The difference would be much greater if hexadecane  $C_{16}H_{34}$  were under consideration.

### *The Motion of a Molecule through the Liquid Mass.*

It is not difficult to imagine that, under such conditions, an aggregation of elastic substances, endowed with enormous amounts of kinetic energy, might diffuse or migrate excessively slowly against the intense fields of force which are consequent on the inter-molecular residual affinities. We cannot conceive of the existence of the excessively slow motion characteristic of the molecules, even in dilute solutions, on any other assumption than the one already made. The motion of a molecule in a liquid mass may be compared to that of the motion of a comparatively large mass (like a projected bullet) through a viscous medium like tar or treacle, as compared with its ordinary motion through the air. The analogy is still

incomplete since the bullet has no affinity for the medium through which it is passing.

It may be remarked in conclusion that a consideration of the molecular volumes from the present point of view is really independent of these theoretical questions, and depends only on the empirical rule that the volumes at the boiling-point are for the most various substances four times the volumes at absolute zero.

It now remains for us to consider how it is that the molecular volumes reflect so accurately the chemical constitutions of substances. In dealing with molecular volumes, it is necessary to take into account such properties as boiling-point, viscosity, and surface tension. We should however note that boiling-points do not always indicate differences in chemical constitution, nor show results which are evident from a study of molecular volumes. For instance variation in molecular volume and boiling-point are not affected to the same degree, by such constitutive features as ring structure.

Dipropargyl $C_6H_6$ .			Benzene.
$CH : C \cdot CH_2 \cdot CH_2 \cdot C : CH$			$C_6H_6$
Volume	111.0	$\Delta - 15.0$	96.0
Boiling-point	85.0	$\Delta - 4.7$	80.3

The variations of the boiling-points for a given chemical change are usually greatly in excess of the volume changes, but not in this case. On the other hand, differences in boiling-point are often accompanied by well-defined changes in volume, but the latter are most frequently in the opposite direction—that is, when the one is positive the other is negative. The intermolecular forces are doubtless of considerable importance in determining the molecular volume, and these may be considered to be determined by the forces of residual affinity arising from the individual atoms. It has been shown that the range of the molecular activity or influence is equal to the distance which separates two molecular centres. The molecular forces influence such physical properties as

(a) *The boiling-point.*—For example, that compound which possesses the highest boiling-point is obviously the most difficult to separate from its neighbours, and to endow with the kinetic energy necessary to cause vaporization. As already stated the effect upon the molecular volume is generally in the opposite direction to that upon the boiling-point. This is seen in such cases as



$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2\text{Cl}$ b.p. $46.5^\circ$ $V_m$ 92.0	$\Delta - 10.0$ $\Delta + 2.3$	$(\text{CH}_3)_2\text{CHCl}$ $36.5^\circ$ 94.3
$\text{CH}_3 \cdot \text{CHBr}_2$ b.p. 111.0 $V_m$ 99.0	$\Delta + 19.3$ $\Delta - 2.0$	$\text{CH}_2\text{Br} \cdot \text{CH}_2\text{Br}$ 130.3 97.0
$p \text{ C}_6\text{H}_4 \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$ b.p. 138.0 $V_m$ 140.2	$\Delta + 3.9$ $\Delta - 2.3$	$m \text{ C}_6\text{H}_4 \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$ 141.9 137.9

The explanation which seems to best suit these cases is that the intermolecular forces are most intense in the higher boiling-point liquids (when two or more isomers are compared), and it is evident that the peculiarity which occasions this difference, is one which favours a more striking manifestation of intramolecular force than in the other case. It is natural then to suppose that the particular combination or spatial association of atoms or groups, or their distribution throughout the molecule, are the factors which cause the differences in the various cases. It should, however, be clearly understood that changes in the boiling-point are not always evidence of corresponding changes in the (*a*) *molecular volumes*, (*b*) *surface tension*, and (*c*) *viscosity*.

It is natural to suppose that boiling-point, surface tension, and viscosity are parallel phenomena, for those influences which tend to increase or diminish one property, also influence the others. Thus we find:—

	b.p.	Viscosity $\eta \times 10^5$ .	Surface tension. $N \times 1000$
n-hexane	68.6	221	
	- 6.6	- 13	
iso-hexane	62.0	208	
xylene <i>o</i>	141	254	16.0
	- 2.0	- 21	- 0.1
xylene <i>m</i>	139	233	15.9
	- 1.0	$\pm 0$	- 0.1
xylene <i>p</i>	138	233	15.8

We see that any explanation of the peculiarities manifested by the molecular volumes of compounds must take into consideration the part intermolecular forces play in determining the molecular volumes of compounds as well as the intramolecular forces themselves. The latter may possibly in some cases be in the same direction as the intermolecular forces, or on the other hand be contrary to them. It probably is not easy to make these distinc-



tions in practice, nor clearly in every case to analyse the complex conditions which obtain. Some constitutive influences are evident enough, such as those of ring structure, the contiguity of groups or separation of groups in dihalogen derivatives of the paraffins, and the ortho, meta, and para modifications of the disubstitution products of benzene, etc. The work which has been done in this volume, whilst to some extent useful for the explanations given of some of the phenomena, is probably of greatest value for the analysis of the effects themselves apart from their causes. The explanations will come later. Even as regards the effects, data are very meagre in many cases, and though the numbers obtained by means of the formula described in Appendix II. may be exceedingly useful as preliminary determinations of data, yet they can never carry the weight of the results of well-directed and well-executed experiments. It is to be hoped that the latter will soon largely increase.

There is no doubt that in spite of the care taken, many parts of the present theory may have to be altered later as data accumulate, and as our knowledge of the physical property increases. The identification and explanation of constitutive effects is not always easy. Some particular atomic values—generally those found in the homologous series  $R-X$  are taken as standard, and by the method of summation the value  $\Sigma nV_a$  is found. The difference  $V_m - \Sigma nV_a$  then measures the constitutive effect. Sometimes a mean atomic value is taken, and it then follows that no account is taken of the variations. The great difficulty is to identify the effect with a particular atom or group. When this seems possible, it sometimes happens that other atoms or groups might equally well be identified with the effect in question. Only a careful examination of a large number of data can overcome these difficulties. It will generally be found that the constitutive effects  $V_m - \Sigma nV_a$  are traceable to some modification in particular atomic values, and a considerable advance is made when we are able to ascertain for certain which atoms are marked by the variation in question, and by how much.

For instance, the contraction for ring compounds like benzene  $C_6H_6$  amounts to  $-15.0$ . Careful inquiry shows that this is made up from a contraction of all the atoms in the nucleus  $C = 12.8$  instead of  $14.8$  and  $H = 3.2$ . It follows that we know the volumes of such residues as  $C_6H_5-$ ,  $C_6H_4=$ , etc., and so are

able to find out the volumes occupied by the side chains. For instance we show that the volume of  $\text{CH}_3$  is the same in the homologues of benzene, if sufficiently separated.

	$V_m$ .	Benz. Rud.	$n\text{CH}_2$ .	$\text{CH}_2$
$\text{C}_6\text{H}_5 \cdot \text{CH}_3$	118.25	92.8	—	25.45
<i>p.</i> $\text{C}_6\text{H}_4 \cdot (\text{CH}_3)_2$	140.51	89.6	50.91	25.45
1:3:5 $\text{C}_6\text{H}_3 \cdot (\text{CH}_3)_3$	162.75	86.4	76.35	25.45

This knowledge may serve as a basis for the determination of the volumes of components of other aromatic compounds and also enable us to measure constitutive effects.

$\text{OC}_6\text{H}_4 (\text{CH}_3)_2$	$V_m$ 137.6	$\text{C}_6\text{H}_4$ 89.6
		$2\text{CH}_3$ 50.9
		<hr/>
		$\Sigma nV_a$ 140.5
		$V_m$ 137.6
		<hr/>
		$\Delta$ For ortho struct. - 2.9
		<hr/>

It happens in this case that  $\Sigma nV_a$  is similar to the volume of *p.* xylene. In other cases this additional information may be lacking, and we depend on the regularity already observed. Greater simplicity is introduced into the work, for our guiding principle by being able to assume that in all these aromatic compounds the phenyl or similar radical, undergoes no change of volume in the different combinations. This enables us to deal with fairly complicated ring compounds.

Much greater difficulty has been experienced with open-chain compounds, owing to our lack of ability to decide which atoms or groups take part in the constitutive effect. This is largely due to the fact that many constitutive effects are more or less affected by the general influence of complexity, which is not dependent on any simple law.

It may also be stated that one reason why the effects may differ somewhat, in degree at any rate, under other conditions than those at the boiling-point, from the effects observed at this point, is just the effect of this temperature factor. We might expect that constitutive effects should be more prominent say at the melting-point than at the boiling-point, because in addition to the diminishing influence of the heat forces, the forces of affinity have increased according to some high power of the distance between the molecular centres, and may even change sign at some point. It is also true that the effects may be different from those observed from the examination of other physical

properties such as refractive power, and magnetic rotatory power for just the reason that they do not possess a temperature factor as do molecular volumes.

In consequence of the facts just mentioned, it is hoped that any deficiencies or irregularities found, will be leniently dealt with, and regarded as part of that unavoidable element of crudity which attaches to all theories in their initial stages.





## APPENDIX I.

### A FORMULA BY MEANS OF WHICH THE MOLECULAR VOLUME AT THE BOILING-POINT MAY BE CALCULATED.\*

IN an extended study of molecular volumes, it was found necessary to calculate some of the values at the boiling-point, and the following formula has been found suitable for this purpose:—

$$\frac{d_0}{d_t} = 1 + c \left( 1 - \frac{273}{\text{B.P.}} \right).$$

The only data necessary are the density at 0° and the boiling-point.

The value of  $c$  is given in the following table, the data being those of Thorpe:—

*Table of Values (Inorganic Compounds).*

Compound.	B.p.	$d_0$ .	$d_{\text{B.p.}}$	$c$ .	$V_m$ . calc.	$V_m$ . obs.	Per cent error.
$\text{S}_2\text{O}_5\text{Cl}_2$ . . .	139·6	1·85846	1·60610	0·460	135·5	135·5	$\pm 0\cdot0$
$\text{SO}_2\text{Cl}\cdot\text{OH}$ . . .	155·3	1·78474	1·54874	0·420	75·5	75·05	+0·7
$\text{SO}_2\text{Cl}_2$ . . .	70·0	1·70814	1·56025	0·462	86·3	86·3	$\pm 0\cdot0$
$\text{AsCl}_3$ . . .	130·2	2·20500	1·91813	0·447	95·1	94·37	+0·76
$\text{AsF}_3$ . . .	60·4	2·6659	2·4497	0·490	53·6	53·84	−0·44
$\text{VOCl}_3$ . . .	127·2	1·86534	1·63073	0·452	106·5	106·2	+0·3
$\text{POBrCl}_2$ . . .	137·6	2·12065	1·83844	0·458	107·5	107·4	+0·1
$\text{PSCl}_3$ . . .	125·1	1·66820	1·45599	0·455	116·3	116·1	+0·2
$\text{POCl}_3$ . . .	107·2	1·71163	1·50967	0·474	101·0	101·4	−0·4
$\text{TiCl}_4$ . . .	136·4	1·76041	1·52223	0·460	124·5	124·5	$\pm 0\cdot0$
$\text{SiCl}_4$ . . .	57·6	1·52408	1·40294	0·500	120·2	120·8	−0·5
$\text{N}_2\text{O}_4$ . . .	21·6	1·49030	1·43958	0·473	64·0	63·9	$\pm 0\cdot0$

Mean value, 0·463.

It is found that by means of the above formula the volumes of compounds of a similar order of complexity can be calculated to within 1 per cent.

Example.— $\text{GeCl}_4$ ,  $d_{18}$  1·887 (Winkler), b.p. 86·0°,  $\frac{273}{T} = 0\cdot760$ ,  $\frac{d_0}{d_t} = 0\cdot46 \times 0\cdot240 = 1\cdot104$ ,  $d_{\text{b.p.}} = \frac{1\cdot887}{1\cdot105} = 1\cdot709$ . M.W. = 213·8;  $V_m$ . 125·1.

Observed, C 14·8, Si 32, Ge [36·3], Sn 42·3, Ti [35·7].

The formula can be used indifferently for inorganic and organic compounds, but the value of  $c$  in the latter varies somewhat as the compounds vary greatly in complexity and the chains lengthen.

\* Adapted from "Journ. Chem. Soc."

The value of  $c$  for organic cyclic compounds without side-chains is similar to the above.

*Cyclic Compounds.*

Compounds.	M.p. or $0^{\circ}$ .	B.p.	$d_t$ $0^{\circ}$ or m.p.	$d_T$ T = B.p.	$c$ .	$V_m$ . calc.	$V_m$ . obs.	Per cent error.
$C_6H_6$ (Benzene) .	$6.0^{\circ}$	$80^{\circ}$	0.8940	0.8133	0.470	95.7	96.0	-0.03
$C_4H_4S$ (Thiophen) .	0.0	84	1.0884	0.9874	0.434	85.5	85.0	+0.6
$C_{10}H_8$ (Naphthalene)	79.2	217	0.9777	0.8674	0.456	147.3	147.2	$\pm 0.0$
$C_{10}H_{14}$ (Hexahydro- naphthalene) .	0.0	200	0.9419	0.7809	0.487	170.0	171.2	-0.7
$C_{14}H_{10}$ (Phenan- threne) .	100.5	340	1.0630	0.9073	0.440	197.8	195.2	+1.3
$C_5H_5N$ (Pyridine) .	0.0	115	1.0033	0.8826	0.462	89.3	89.3	$\pm 0.0$
$C_9H_7N$ (Quinoline) .	0.0	234	1.1081	0.9211	0.439	141.1	140.0	+0.8
Mean value, 0.460.								

The results of calculation show very fair agreement with observation, and thus giving a fairly trustworthy method for the calculation of unknown values.

*Example.*—*Hydrindene*,  $C_9H_{10}$  :  $d_5$  0.957, b.p.  $176^{\circ}$ ,  $c = 46$ ,  $V_m$  144.0.  $\Sigma nV_a = (4 \times 9 + 10)3.7 = 46 \times 3.7 = 170.2$ ,  $\Delta = -26.2$  for ring. Contraction for 1 six-membered ring + 1 five-membered ring =  $-15 - 11.5 = -26.5$ .

*Acenaphthene*,  $C_{12}H_8$ .—The value of  $c$  for phenanthrene is 0.440. For acenaphthene,  $d_{103}$  1.030, m.p.  $103^{\circ}$ , b.p.  $277^{\circ}$ .  $V_m$  166.6,  $\Sigma nV_a$  207.2,  $\Delta = -40.6$ . Contraction for 2 six-membered rings + 1 five-membered ring =  $-30.0 - 11.5 = -41.5$ .

The only difficulty is met with in open-chain organic compounds.

For compounds like chloroform, carbon tetrachloride, and trichloromethane, the value of  $c$  mentioned above (0.460) may suffice.

$c$ , in general, increases by 0.024 for every addition of  $CH_2$  in open-chain compounds, thus :—

$$\begin{array}{ccccccc} C_5H_{12} & 0.476, & C_6H_{14} & 0.500, & C_7H_{16} & 0.532, & C_8H_{18} & 0.554, \\ & \Delta & 0.024 & & 0.032 & & 0.022 & \end{array}$$

When considering an unknown value for a certain compound, it is usually possible to find an analogous compound from which  $c$  may be calculated, for example, cymene,  $C_{10}H_{14}$ , for the terpenes (menthane),  $C_{10}H_{16}$ , methyl succinate for methyl maleate or fumarate, propionitrile for ethyl carbylamine, and ethyl nitroethane for ethyl nitrite.

## APPENDIX II.

### AN INVESTIGATION OF THE DICARBOXYLIC ESTERS.

WHILST this work was passing through the press, a successful investigation was made of the dicarboxylic esters, a series which for a long time resisted treatment. They show quite a number of points of interest, especially of the influence of complexity, so that it will be useful to include them in an appendix at the end of the volume.

We find that the *oxalates* and *formates* show many points of similarity, whilst the *malonates* and the *succinates* compare with the acetates.

From the formates.

$$\begin{aligned} & -\text{COOCH}_3 \\ 62.7 - 4.0 &= 58.7 \end{aligned}$$

$$\begin{aligned} & -\text{COOC}_2\text{H}_5 \\ 84.6 - 4.0 &= 80.6 \end{aligned}$$

Dimethyl oxalate.

$$\begin{aligned} & V_m \cdot (\text{COOCH}_3)_2 \\ &= 2 \times 58.7 = 117.4 \\ & \text{Observed } 117.4 \end{aligned}$$

Methyl ethyl oxalate.

$$\begin{aligned} & \begin{array}{c} \text{COOCH}_3 \\ V_m | \\ \text{COOC}_2\text{H}_5 \end{array} \\ &= 58.7 + 80.6 = 139.3 \\ & \text{Observed } 139.4 \end{aligned}$$

From the acetates.

$$\begin{aligned} & -\text{COOCH}_3 \\ 83.2 - 25.9 &= 57.3 \end{aligned}$$

$$\begin{aligned} & -\text{CH}_2 \cdot \text{COOCH}_3 \\ 83.2 - 4.0 &= 79.2 \end{aligned}$$

Dimethyl malonate.

$$\begin{aligned} & \begin{array}{c} \text{COOCH}_3 \\ V_m \text{ CH} \diagup \diagdown \\ \text{COOCH}_3 \end{array} \\ &= 79.2 + 58.7 = 137.9 \\ & \text{Observed } 137.9 \end{aligned}$$

*The Oxalates* (Wiens Königsberg Inaug. Diss., 1887).

	$V_m$ .	$\Sigma_n V_a$ .	For complexity + $n \times 3.3$	Calc.
$\begin{array}{c} \text{COOCH}_3 \\   \\ \text{COOCH}_3 \\   \\ \text{COOCH}_3 \end{array}$	117.4	117.4	—	117.4
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\   \\ \text{COOC}_2\text{H}_5 \end{array}$	139.4	139.4	—	139.4
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\   \\ \text{COOC}_3\text{H}_7 \end{array}$	162.2	161.8	—	161.8
$\begin{array}{c} \text{COOC}_3\text{H}_7 \\   \\ \text{COOC}_3\text{H}_7 \end{array}$	215.8	$\begin{array}{c} 205.4 \\ 117.4 + 4 \times 22.0 \end{array}$	$\begin{array}{c} 3 \times 3.3 \\ 9.9 \end{array}$	215.3
$\begin{array}{c} \text{COOC}_3\text{H}_7 \\   \\ \text{COOC}_7\text{H}_{11} \end{array}$	316.5	293.4	$\begin{array}{c} 7 \times 3.3 \\ 23.1 \end{array}$	316.5

$\begin{array}{c} \text{COOC}_3\text{H}_7 \\   \\ \text{COOC}_8\text{H}_{17} \end{array}$	341.9	315.4	$8 \times 3.3$ 26.4	341.8
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*The Malonates.*

$\begin{array}{c} \text{COOCH}_3 \\   \\ \text{CH}_2 \\   \\ \text{COOCH}_3 \\   \\ \text{COOC}_2\text{H}_5 \end{array}$	137.9	137.9	—	137.9
$\begin{array}{c} \text{CH}_2 \\   \\ \text{COOC}_2\text{H}_5 \end{array}$	185.6	181.9 137.9 + 44.0	$1 \times 3.3$	185.2
$\begin{array}{c} \text{COOC}_3\text{H}_7 \\   \\ \text{CH}_2 \\   \\ \text{COOC}_3\text{H}_7 \end{array}$	235.0	225.9	$3 \times 3.3$ 9.9	235.8

*The Succinates.*

$\begin{array}{c} \text{CH}_2\text{—COOCH}_3 \\   \\ \text{CH}_2\text{—COOCH}_3 \\   \\ \text{CH}_2\text{—COOC}_3\text{H}_7 \\   \\ \text{CH}_2\text{—COOC}_3\text{H}_7 \end{array}$	160.0	248.0 160 + 4 × 22.0	$3 \times 3.3$ 9.9	257.9
$\begin{array}{c} \text{CH}_2\text{—COOC}_2\text{H}_5 \\   \\ \text{CH}_2\text{—COOC}_3\text{H}_7 \end{array}$	232.0	226.0	$2 \times 3.3$ 6.6	232.6
$\begin{array}{c} \text{CH}_2\text{—COOC}_2\text{H}_5 \\   \\ \text{CH}_2\text{—COOC}_7\text{H}_{15} \end{array}$	333.6	314.0	$6 \times 3.3$ 19.8	333.8
$\begin{array}{c} \text{CH}_2\text{—COOC}_7\text{H}_{15} \\   \\ \text{CH}_2\text{—COOC}_7\text{H}_{15} \end{array}$	460.6	424.0	$11 \times 3.3$ 36.3	460.3

The rule for increase due to complexity in the case of Wien's compounds is: *Add 22.0 for every CH<sub>2</sub> added after the simple methyl compounds, and an additional 3.3 for every CH<sub>2</sub> added beyond 3CH<sub>2</sub>.* One observation of some significance is, that the increase due to complexity is rectilinear. This has been found to be the case in the

$$\left\{ \begin{array}{l} \text{Acrylic esters } \text{CH}_2 = \text{CH—COOR} \\ \text{Phenolic ethers } \text{C}_6\text{H}_5\text{—OR and other aromatic esters} \\ \text{Dicarboxylic esters } (\text{COOR})_2, \text{CH}_2(\text{COOR})_2, \text{C}_2\text{H}_4(\text{COOR})_2. \end{array} \right.$$

On the other hand we find that in the case of the aliphatic ethers R—O—R<sup>1</sup> the augmentation depends upon the *square* of the complexity.

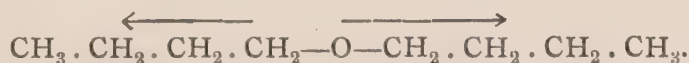
These effects are probably due to the following features. In the



first series, the augmentation only affects the hydrocarbon (paraffinoid) radicals R, and since the saturated carbon chain extends only on one side, the augmentation depends on the complexity simply.



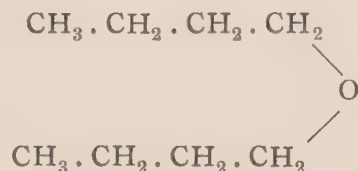
In the aliphatic ethers the augmentation depends on the *square of the complexity*, because the saturated carbon chain extends on both sides of the oxygen atom.



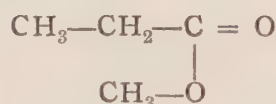
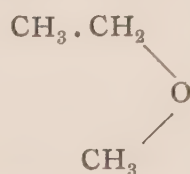
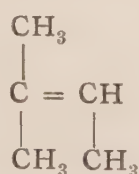
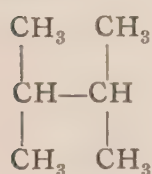
There are indications that this is also the case in the symmetrical normal paraffins.



If the radicals on one side are substituted, or if the phenyl or other similar radical replace the saturated aliphatic radical, so rendering the compound non-symmetrical, the simple rule obtains. If, however, there be a symmetrical arrangement on both sides the rule is more complex. *This more complicated rule suggests interaction between the two radicals.* This might be the case if the arrangement of the atoms were as in the scheme.

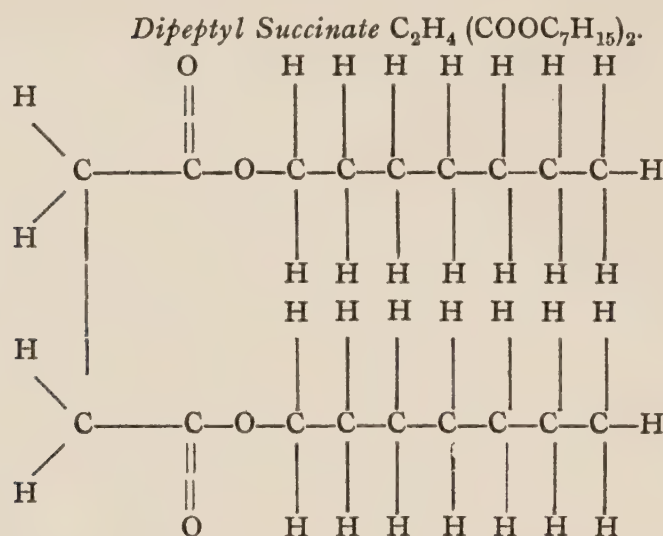


The facts in favour of the disposition of the oxygen valencies shown by  $\diagup \text{O} \diagdown$  are numerous. Considerable differences in the complexity of the two radicals generally cause a diminution however. This suggests important modifications in the configuration of oxygen compounds or rather they show that the configurations follow from a similar law to that which governs the tetrahedral arrangement of groups about the carbon atom.



In all these cases there are augmentations in the boiling-point and diminutions in the volume.

It is noticed that among Wiens' compounds is the di-heptyl succinate, which contains no fewer than 53 atoms and the very large molecular volume of 460 c.c. or nearly 500 c.c. This is the largest molecule with which we have had to deal in the course of this investigation.



Finally it should be stated that some of Wiens' numbers differ unaccountably from the expected values.

	$V_m$ .	$\Sigma_n V_a$ .	$\Delta$ .
$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \diagup \\ \text{CH}_2 \\ \diagdown \\ \text{COOC}_3\text{H}_7 \\ \text{COOC}_4\text{H}_9 \end{array}$	208.2	210.5 *	-2.3
$\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{COOC}_4\text{H}_9 \\ \diagdown \\ \text{CH}_2-\text{COOC}_3\text{H}_7 \\   \\ \text{CH}_2-\text{COOC}_4\text{H}_9 \end{array}$	280.0	286.4	-6.4
$\begin{array}{c} \text{CH}_2-\text{COOC}_3\text{H}_7 \\   \\ \text{CH}_2-\text{COOC}_4\text{H}_9 \end{array}$	278.4	283.2	-4.8

It is at present impossible to account for these differences. They are far larger than any probable error due to faulty experiment or even to impurity of liquid. Another very remarkable feature is that Weger gives data which are somewhat different to those which might be expected from Wiens' results, and yet show a regularity so far as the increase due to complexity is concerned. The compounds are succinates.

	$V_m$ .	$\Sigma_n V_a$ .	For complex calc. (Wiens).		
$\text{CH}_2-\text{COOCH}_3$	160.0	—	—	—	—
$\begin{array}{c}   \\ \text{CH}_2-\text{COOCH}_3 \\   \\ \text{CH}_2-\text{COOCH}_3 \end{array}$	(Weger)	—	—	—	—
$\begin{array}{c}   \\ \text{CH}_2-\text{COOC}_2\text{H}_5 \\   \\ \text{CH}_2-\text{COOC}_2\text{H}_5 \end{array}$	185.0	182.0	$1 \times 3.3$	185.3	182.0
	(Weger)			$\Delta 3.3$	
$\begin{array}{c}   \\ \text{CH}_2-\text{COOC}_2\text{H}_5 \\   \\ \text{CH}_2-\text{COOC}_2\text{H}_5 \\   \\ \text{CH}_2-\text{COOC}_3\text{H}_7 \end{array}$	210.3	204.0	$2 \times 3.3$	210.6	207.3
	(Weger)			$\Delta 3.3$	
$\begin{array}{c}   \\ \text{CH}_2-\text{COOC}_3\text{H}_7 \\   \\ \text{CH}_2-\text{COOC}_3\text{H}_7 \end{array}$	257.2	248.0	$3 \times 3.3$	261.2	257.9
	(Wiens)			$\Delta 3.3$	

\* This is the volume of the isomeric ethyl succinate  $C_2H_4(COOC_2H_5)_2$  according to Weger.

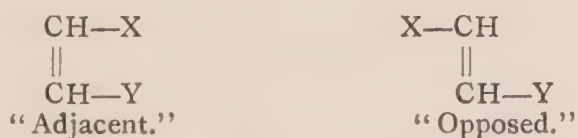
In the first three cases Wiens' results are 3.3 units smaller than those of Weger, but in the fourth case which was determined by Wiens, the latter regularity applies and Weger's regularity shows a result 3.3 too high. These facts, taken together with the anomalous results due to Wiens which show differences equal to 3.3 or some multiple thereof, leave us with the impression that these augmentations for some reason unknown may in part fail. The principle involved is that a liquid substance, which so far as we know, is the same structurally, may possess two or more values, and that thus the volume of liquids may be variable for unknown reasons. A similar case, is when a substance assumes the liquid state, whereas the temperature conditions demand that it should be a solid. The condition is, however, an unstable one, and slight causes will lead to ordinary conditions. Another case is that of a liquid which shows a variable surface tension owing to slight amounts of impurity. In the light of this, we might suppose that the intermolecular forces are also capable of being rendered latent and inoperative for a similar reason.

A comparison of the boiling-points show considerable irregularities. This might be expected to be the case.

The regularity demanded by Weger's results nearly all show an augmentation after the *methyl compound* in the case of the esters. Wiens' results all show an augmentation after the *third carbon atom* in the radicals. There is thus a constant difference of about 3.3 between Weger's results and those due to Wiens.

#### *The Volumes of Geometrical Isomers.*

It will now be interesting to calculate the volumes of a number of geometrical isomers, constructed according to the well-known malenoid and fumaroid types.



In order to do this, we need to know the values of *c* for the corresponding saturated compounds. The data for the dicarboxylic esters give us the necessary means of doing this and so of solving the problem.

The compounds open to investigation are :—

“Adjacent.”	“Opposed.”
Ethyl maleate.	Ethyl fumarate.
$\text{C}_8\text{H}_{12}\text{O}_4$ b.p. 225.0	b.p. 206.2
$d_{20}$ 1.06917	$d_{20}$ 1.05200
Propyl maleate.	Propyl fumarate.
$\text{C}_{10}\text{H}_{16}\text{O}_4$ b.p.	b.p.
$d_{20}$ 1.02899	$d_{20}$ 1.02203
Methyl maleate.	
$\text{C}_6\text{H}_8\text{O}_4$ b.p. 205	
$d_{20}$ 1.15172	



Methyl succinate.	B.p.	$d_0$ .	$d$ B.p.	C.
$C_6H_{10}O_4$	195.2	1.1162 ( $d_{18}$ )	0.912	0.59
Ethyl succinate.				
$C_8H_{14}O_4$	215.4	1.0596	0.82726	0.635
Ethyl propyl succinate.				
$C_9H_{16}O_4$	231.0	1.03866	0.81476	0.658
Ethyl butyl succinate.				
$C_{10}H_{18}O_4$	247	1.02178	0.78572	0.639

Applying these values we find :—

Methyl succinate.			Methyl maleate.
$CH_2-COOCH_3$			$CH-COOCH_3$
	$\Delta$		
$CH_2-COOCH_3$			$CH-COOCH_3$
b.p. 195.2° $V_m$ 160.0	—6.5		153.5 b.p. 205°
Ethyl succinate.			Ethyl maleate.
$CH_2-COOC_2H_5$			$CH-COOC_2H_5$
$CH_2-COOC_2H_5$			$CH-COOC_2H_5$
b.p. 215° $V_m$ 210.3	—7.0		203.3 b.p. 225°
Propyl succinate.			Propyl maleate.
$CH_2-COOC_3H_7$			$CH-COOC_3H_7$
$CH_2-COOC_3H_7$			$CH-COOC_3H_7$
b.p. 247° $V_m$ 258.4	—8.4		250.0 b.p. 257°

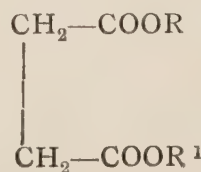
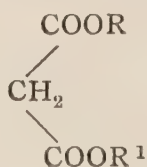
*The Fumarates.*

Ethyl fumarate $C_8H_{12}O_4$ .	
$C_2H_5OOC-CH$	
$HC-COOC_2H_5$	
b.p. 218° $d_{20}$ 1.05200	
$V_m$ 204.5	
	$\Delta + 1.2$
Ethyl maleate 203.3	
Propyl fumarate $C_{10}H_{16}O_4$ .	
$C_3H_7.OOC-CH$	
$HC-COOC_3H_7$	
b.p. 250° $d_{20}$ 1.02203	
$V_m$ 250.8	
	$\Delta + 0.8$
Propyl maleate 250.0	

It is seen that the *maleic esters* differ from the corresponding succinic esters by about the volume of  $H_2 = 7.2$  which represents their difference in composition.

The *fumaric esters* are about a unit larger.

We might expect the former to manifest the above differences. At any rate it shows that the succinic and no doubt the malonic and oxalic esters are constructed according to the adjacent types.









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PRINTED IN GREAT BRITAIN BY THE UNIVERSITY PRESS, ABERDEEN













